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**Exploratory Study of the Decomposition and Combustion Process of Ionically
Conducting Gel and Solid Propellants**

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Exploratory Study of the Decomposition and Combustion Process of Ionically Conducting Gel and Solid Propellant

ABSTRACT

On demand control of propellants and energetic materials in general is of great interest and importance. In this work, we systematically studied the electrochemical decomposition of solid oxidizers. Then, we synthesized and characterized polymer electrolyte propellants in both gel and solid form. We have identified key pathways for ignition and throttling of propellant combustion. In addition, we have identified compositions which will extinguish when electrical power is removed even at elevated pressure. Finally, we explored the role of additives in terms of ignition, combustion, and quenching of propellants.

Research Objectives

The primary objective of this research is to gain a fundamental understanding of the condensed phase decomposition and combustion behavior of commonly used salts in propellants and explosives as well as solid propellants and gelled monopropellants. The condensed phase will be subjected to electrical stimulation in an effort to begin an initiation process and or actively alter the steady state combustion process. Initially studies will consider propellant components separately combusting at atmospheric pressure. The project will then progress to studying propellants at atmospheric pressure, and finally the influence of pressure will be examined.

The potential end benefits of this research include 1) development of ignition system allowing a solid propellant to be started-stopped-and restarted repeatedly, 2) throttling of solid propellants, 3) an active

control system for solid propellant combustion instability, and 4) gelled monopropellants suitable for micropropulsion thrusters.

Accomplishments

Within this effort, there were a total of 6 studies that are detailed below. The first study involved neat and blended oxidizers, and is designated with an “O” in the following section. Two studies involved gel polymer electrolyte propellants. They are designated as “G1” and “G2” respectively in the following section. Finally, there were 3 studies involving solid propellants, and they are designated as “S1”, “S2”, and “S3” respectively.

Oxidizer Study “O”

The solid oxidizers under consideration in this study were AN, LP, and AP. AN was purchased from Sigma-Aldrich and had a purity of over 99.0%. The AP used was 200-micron mesh particle size and was purchased from Pyro Chem Source. LP was purchased from Firefox Enterprises and was 100-micron mesh particle size and over 99.2% purity. In order to create consistent samples, they were prepared by first placing the loose oxidizer powder in a vacuum at 40°C overnight to remove any moisture which may have adsorbed onto the surfaces during storage. In total, four sample types were considered, as shown in Table 1, including 100 wt.% AN, 100 wt.% LP, and two blends of LP and AP. For the blends, the oxidizers were combined and stirred to ensure sufficient mixing of the components. Once prepared, samples were pressed into pellets with a nominal mass of 1.5 g in a 10 mm diameter die for 1 minute at a load of 5 tons. The mixture ratio and the mean and standard deviation density characteristics of the samples created are outlined in Table O.1.

O.1 Regression Rate Experiments

Previous work conducted by Young et al. (2013) on the diffusion flames of solid oxidizers with gaseous fuels revealed a very thick melt layer associated with AN combustion. In order to take advantage of the opportunity to probe this thick melt layer, a similar approach was taken in this study. A modified counterflow burner was designed and fabricated based on a previous design, the details of which can be found in Young et al. (2010). Due to the desire to apply electrical power to the system, the modified counterflow burner was fabricated from G10 Garolite because of its nonconductive and flame-retardant properties. A schematic diagram of the counterflow burner is shown in Fig. O.1.

To summarize the use of the counter flow burner, a solid oxidizer pellet was loaded into the apparatus and held in place by a thin nichrome wire and linear variable displacement transducer (LVDT). The LVDT had the dual purpose of applying pressure to the base of the oxidizer pellet, ensuring the top of the pellet is held at a fixed location, along with tracking the regression rate. The regression rate was found from calculating the slope of the displacement plot, as shown in Fig. O.2, using the change in displacement (y) and time (t) between two points at the area with the displacement change over the time of interest, as illustrated by the boxed area.

A series of unpowered experiments were conducted to develop a baseline and to use as a verification of our results and processes in comparison to previous research (Young et al., 2013). Our baseline corresponds to the lowest strain rate condition in that work (Young et al., 2013).

Table O.1: Sample characteristics

Oxidizer Identification	Weight Percentages of Components	Density of Oxidizer Pellets (g/cm³)	Percent Theoretical Max Density
SO1	100% AN	1.64 ± 0.036	96%
SO2	100% LP	2.23 ± 0.049	92%
SO3	50% LP/50% AP	2.04 ± 0.033	93%
SO4	20% LP/80% AP	1.94 ± 0.021	97%

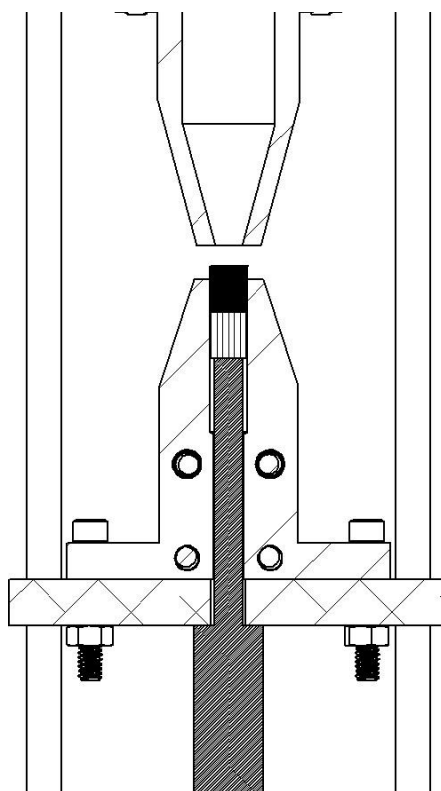


Fig. O.1: Schematic of counter flow burner

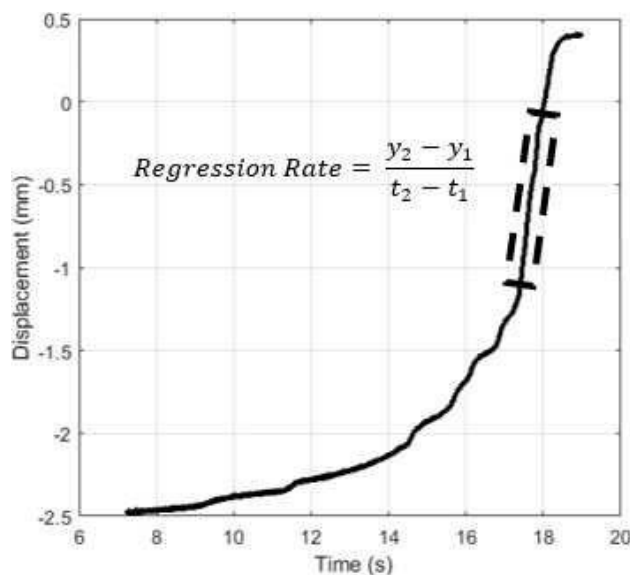


Fig. O.2: Regression rate calculation

The main area of focus of this research was to analyze the effect an applied voltage potential had on the solid oxidizer pellet samples. These experiments were carried out similar to the counter flow burner experiments described in the previous section. The main difference was that the nichrome wire was replaced with electrodes, which now served the purpose of holding the sample in place and conducting the applied power to the solid oxidizer. In all of the experiments, the electrodes had a diameter of 0.5 mm. The majority of the experiments were conducted with copper electrodes, while several additional experiments were conducted using platinum wires for comparison.

The applied power experiments were carried out by loading the desired solid oxidizer sample pellet into the experiment stand and applying the electrodes across the top of the sample. The electrodes were spaced approximately 5 mm from each other and placed to ensure the pellet was sitting level in the burner. From the earlier work of Khoruzhii and our initial experiments during which no notable reaction took place, it was assumed that the oxidizers in their solid state were nonconductive (Khoruzhii et al., 2007, 2008). For this reason, the gaseous fuel was used to create a flame with the solid oxidizer pellet for long enough to fully form a melt layer. Once the melt layer was formed, the gas fuel was turned off and the Harrison 6274A DC power supply was turned on with the desired voltage, then the regression rate, voltage, and current draw were recorded, as shown in Fig. O.3. The current draw was measured using a Fluke i50s current probe, which was connected to a National Instruments SCB-68A data acquisition unit (DAQ). The DAQ also measured the displacement of the LVDT and voltage applied. All data was collected on a PC using a custom LabVIEW VI. The regression rate was found using the same method shown in Fig. O.2, using the slope of the displacement plot. For the range selected in the regression rate calculation, the average of the current and voltage values was extracted from the raw data.

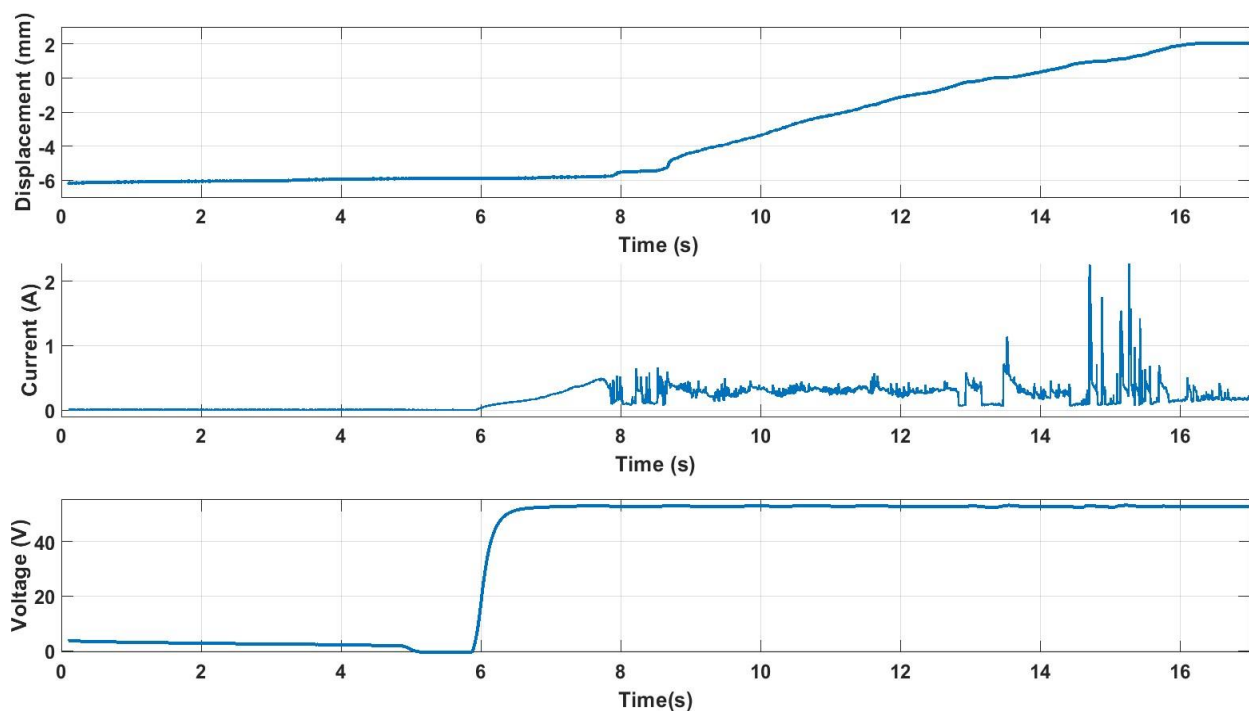


Fig. O.3: Example of applied power test results for displacement (top), current draw (middle), and voltage applied (bottom)

Figure O.3 is representative of the procedure for all applied power tests. Initially, no power was applied, as shown by the zero-voltage value in the voltage plot of Fig. O.3, while the flame was providing sufficient heat to the oxidizer to create a liquid melt layer. In this example, at six seconds, the power was turned on while the gaseous fuel was turned off. The applied voltage caused the melt layer to grow, and current began to flow a short while later, as shown by the rise in the current plot. Once the melt layer was fully formed and the current draw became substantial, an accelerated reaction took place, as shown by the increased slope of the displacement plot at eight seconds. It should be pointed out that for an unpowered case, the gaseous fuel flow must remain on. The diffusion flame between the gaseous fuel and oxidizer was required to create the heat feedback for a self-sustaining system. Without the gaseous fuel flow, the solid oxidizer quenches. However, in the powered cases, once power was supplied, the reaction was self-sustaining, and the fuel flow was removed. The experiments were also recorded using a Phantom VEO 7.10L high-speed camera to provide visual insight on the decomposition of the oxidizer and the interaction of the melt layer with the electrodes.

Further experiments outside of the counter flow burner were carried out to evaluate the change in the conductivity and electrical resistance of the samples when they are in solid phase compared to their liquid melt phase. This was done by determining the resistance from the measured voltage and current values in the applied power diffusion flame experiments. To gain an understanding of the resistance in the solid phase of the oxidizers, pellets of each oxidizer composition had two platinum wire electrodes placed across the top face of the solid pellet. A voltage sweep from -12 V to 12 V was carried out, and the resulting current was measured using a Solartron Analytical 1287 Electrochemical Interface. Using the cross-sectional area

(A), distance between the electrodes (L), current (I), and voltage (V), the resistivity (ρ), and resistance (R) are defined as

$$R = \frac{V}{I} \quad (\text{O.1})$$

$$R = \rho \frac{L}{A} \quad (\text{O.2})$$

The resistance in the liquid melt layer was found by using the measured voltage and current for each of the applied power experiments. The change in resistance between the solid and liquid phases of each of the oxidizers was compared to gain an understanding of the change in conductivity, which is the inverse of the resistivity, accompanying the phase change.

O.2 RESULTS AND DISCUSSION

O.2.1 Solid Oxidizer Interaction with Applied Power

The application of power to the solid oxidizer samples studied resulted in a larger and much more active melt layer in comparison to the unpowered experiments. As seen in Fig. O4, during experiments with pure AN with a gaseous fuel and no power applied, the melt layer formed a cloudy hemisphere. When power was applied, as seen in the second image of Fig. O4, the melt layer became much larger and had a substantially higher concentration of gas inside the melt layer, as evidenced by the increase of bubbles. If the power was turned off, the system would quench, and no further reaction would occur. The power supplied into the system facilitates the decomposition through an electrocatalyzed initiation step that causes AN to break down into an anion (NO_3^-) and a cation (NH_4^+), as shown in Eq. (O.3). These decomposition products are then reduced, as shown in Eqs. (O.4) and (O.5) (Dong et al., 2016; Johnson and Yerhoff, 1987). Rather than being white or translucent, as in the unpowered case, when powered the melt layer turned blue when copper metal was used as the electrode material. This blue color resulted from the copper ions complexing with ammonia from AN (Royal Institute of Technology, Stockholm, 2000).

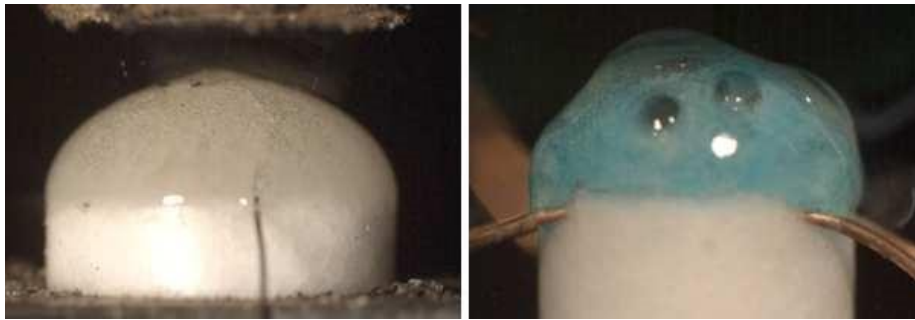


Fig. O.4: AN melt layer unpowered experiment (left) and powered experiment (right)



According to the copper Pourbaix diagram, solid copper is reduced into Cu^{2+} in an acidic environment, as that caused by the nitric acid, which is an AN decomposition product. (Gambino et al., 2008; Chaturvedi and Dave, 2013). These Cu^{2+} can react with various AN decomposition products to form a range of products such as $\text{Cu}(\text{NH}_3)_4^{2+}$ or $\text{Cu}(\text{H}_2\text{O})_5(\text{NH}_3)_4^{2+}$, which are exothermic reactions (Royal Institute of Technology, Stockholm, 2000).

Figure O.5 shows the evolution of the melt layer between the electrodes for the AN at 50 V. The time $t = 0$ s does not signify the start of power application but is the relative starting point to illustrate the time scale in the melt layer formation. As seen in Fig. O.5 at $t = 0$ s, there is a slight blue melt layer around the cathode, and it is much larger around the anode. At $t = 0.4$ s, the melt layers between the anode and cathode have grown enough to begin to make contact with each other. At $t = 0.7$ s, substantial contact has been made, and it can be clearly seen that a significantly larger amount of bubbles and gas are being formed. Once the contact between the electrodes is sizable, the reaction accelerates greatly, as shown at $t = 1$ s. At $t = 1$ s, the melt layer has become significantly larger, accompanied by much more gaseous decomposition products, which first appear at the cathode.

Due to the clear reaction that occurs with the oxidizer and the copper wire, experiments were also carried out using platinum wire as the electrodes. Platinum is chemically inert, does not oxidize easily, and is resistant to acids, so it should not react with the samples during the experiments (Berkeley Rausser College of Natural Resources, n.d.). As seen in Fig. O.6, using copper as the electrodes resulted in a large blue melt layer that has a large concentration of bubbles. Using the platinum electrodes caused a smaller clear melt layer that still had a large amount of gas present. Due to the platinum not being dissolved into the solution, the key reaction taking place is the break down of AN into its anion and cation and the reductions that follow, as shown in Eqs. (O.3)–(O.5). This shows that the material used for the electrodes has an effect on the reactions that occur with AN. Regardless of the electrode material selected, most activity started at the anode, which was often completely consumed when copper was used. The anode is where oxidation occurs in electrochemistry, so it is expected that the copper anode would be consumed at a faster rate than the cathode (Sawyer, 2003). The electrochemical decomposition initiation step of AN and further reduction is believed to proceed at a much faster rate than the proton transfer initiation step that is present in thermal decomposition of AN, which leads to a higher regression rate (Chaturvedi and Dave, 2013).

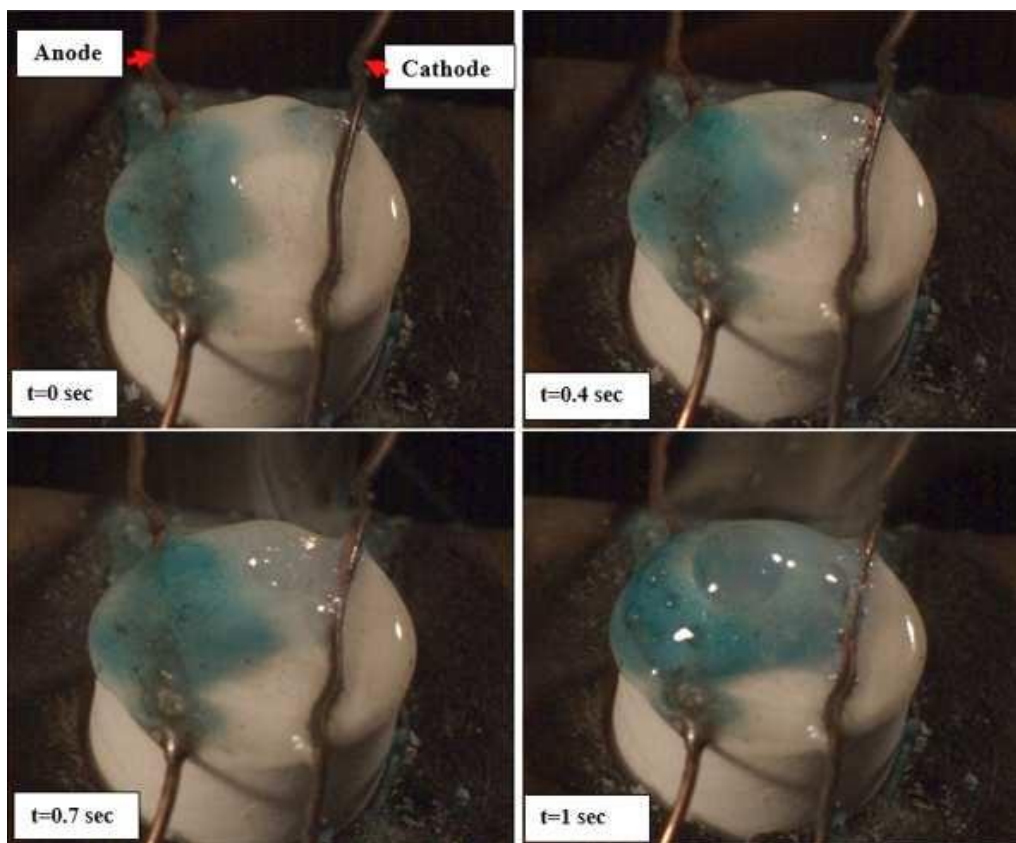


Fig. O.5: Melt layer development between electrodes

A similar trend was observed when the experiments were conducted with the LP oxidizer samples. When the power was applied to the LP samples, the melt layer became substantially more active compared to when the gas fuel was used. As seen in Fig. O.7, the copper electrodes caused a black melt layer, which was believed to be copper oxide resulting from a reaction with the oxygen in the LP decomposition, defined as (Zhang et al., 2015; Purdue University Division of Chemical Education, n.d.; Anders and Plambeck, 1968):

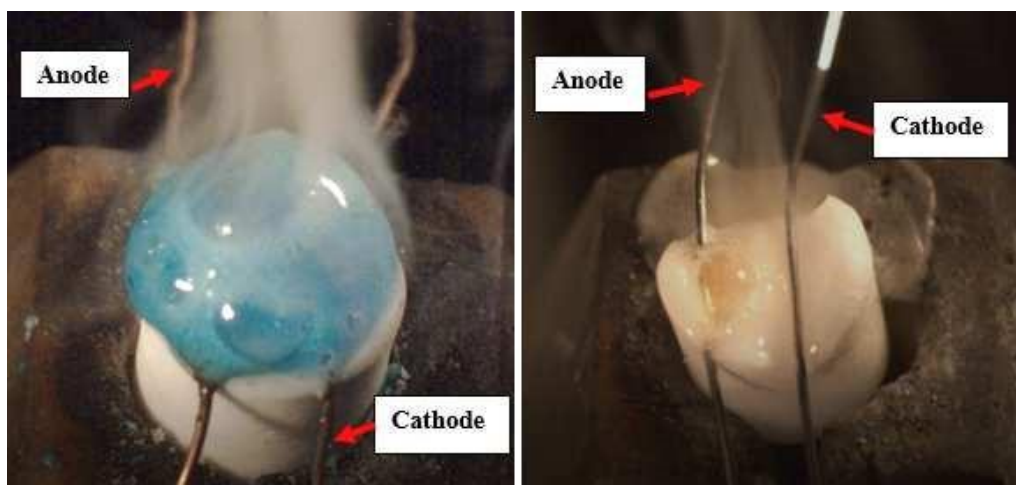


Fig. O.6: AN decomposition with copper (left) and platinum (right) electrodes

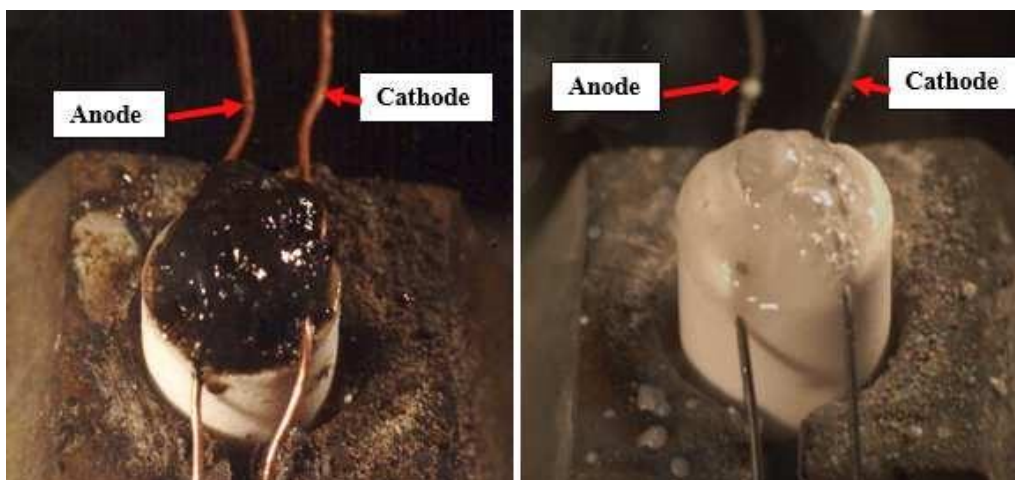


Fig. O.7: LP decomposition with copper (left) and platinum (right) electrodes



The reaction in Eq. (O.10) to create copper oxide is an exothermic reaction that produces 312 kJ/mol of heat. Prior research in using copper electrodes in molten lithium perchlorate found that the copper oxide formed directly on the copper surface (Denning and Johnson, 1967). As shown in Fig. O.7, the platinum wire did not substantially react with the LP, similar to what was observed with AN. This inert nature of platinum leads to Eqs. (O.7) and (O.9) being the driving reactions taking place when platinum electrodes are used. Similarly, the anode was where the reaction appeared to start in the LP reaction and was often completely consumed when copper was used as the electrode material. The lithium deposition in Eq. (O.8) is endothermic, requiring 280 kJ/mol of heat, while the perchlorate decomposition in Eq. (O.9) is exothermic and produces 36 kJ/mol of heat.

O.2.2 Effect of Applied Power on Regression Rate

In all of the powered experiments, a DC voltage potential was applied across the top of the sample. As shown in Fig. O.8, with the exception of SO4 (80% AP/20% LP), the regression rate of each oxidizer increased significantly with the magnitude of the applied DC voltage. SO4, which contained the highest concentration of AP, exhibited the smallest melt layer of all of the samples. Pure AP has a melt layer of around 1 μ m at atmospheric pressure, similar to the conditions in which the experiments were being conducted (Jung and Yoh, 2010). Whereas in the case of AN, the melt layer is approximately 3mm thick, and similar melt layer sizes were observed in the pure LP cases run in atmospheric conditions (Young et al., 2013). The conductive melt layer is the driving factor allowing for the power to conduct and the reaction to take place. Therefore, a small melt layer may inhibit the process slightly (Khoruzhii et al., 2007, 2008). While the general trend is for the regression rates to increase with increasing applied voltage, there is a fair amount of scatter within the data. The scatter observed in Fig. O.8 is due to the chaotic nature of the melt

layers once the voltage is applied. As seen in Figs. O.6 and O.7, the melt layers become very active with a large amount of bubbles formed. These bubbles and the constant changing of the shape of the melt layer causes the contact with the electrodes to change, as well as the conductivity of the melt layer itself to change from one point in the experiment to another. The error bars shown in Fig. O.8 represent the measurement error for an individual experiment as determined by the manufacturer linear displacement tolerance in the LVDT and voltage reading tolerance by DAQ.

As Fig. O.8 shows, SO1 exhibited the greatest regression rate sensitivity to the applied voltage, as evidenced by the greatest slope. In the unpowered case, SO1 demonstrated an average regression rate of 0.045 mm/s, compared to 1.41 mm/s when 50 V was applied with the copper electrodes. This is a regression rate increase of over 30 times. SO1 also had the highest average regression rate of all the samples studied.

Pure LP (SO2), exhibited a similar trend as SO1 but with an overall lower regression rate and a lower sensitivity to the applied voltage, as shown in Fig. O.8. This was likely due to the fact that LP has a large well-defined melt layer, so contact with the electrodes is strong, but the pure LP sample is regarded as a low-energy oxidizer (Missile Technology Control Regime, 2017). By comparing SO2 in the unpowered state (average regression rate of 0.017 mm/s) to the regression rate at 50 V with copper electrodes (0.99 mm/s), an increase in magnitude of over 58 times was observed. Even with this large increase in the regression rate, this sample ended up having the lowest regression rate of all samples studied.

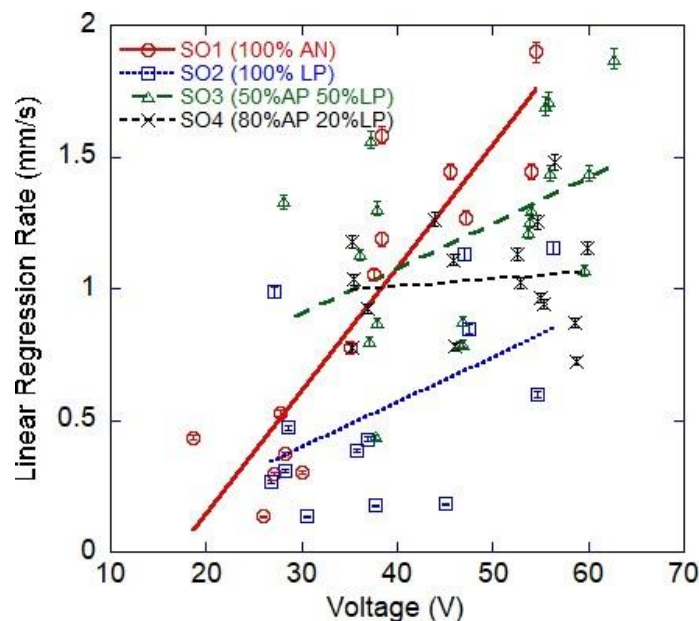


Fig. O.8: Applied voltage vs. regression rate with copper electrodes

Energetically, LP is not highly desirable compared to other potential oxidizers. In order to increase the available energy while still producing a substantial melt layer, LP was blended with AP. Considering SO3 (50% AP/50% LP), the relationship between the applied voltage and the regression rate remained significant. This was likely due to the fact that the melt layer size remains substantial due to the LP, and therefore good contact with the electrodes was achieved. The average unpowered regression rate of SO3 was found to be 0.020 mm/s, which was substantially less than the 1.13 mm/s average regression rate when 50 V was applied using copper electrodes. This equates to a 56 times increase in regression rate over the voltage range considered.

Increasing the concentration of AP even further, as with SO4 (80% AP/20% LP), causes the relationship between the applied voltage and regression rate to become weaker compared with the other samples. As seen in Fig. O.8, the trend line of the voltage versus regression rate is nearly horizontal, which was likely due to a smaller melt layer. A smaller melt layer results in a more resistive melt layer, as the contact area becomes more sensitive to melt layer disruptions. Even with a small melt layer in the SO4, a substantial increase in the average regression rate was observed. The base line average regression rate of 0.037 mm/s was found using ethylene and no power applied. This was substantially less than the average regression rate of 1.16 mm/s when 50 V was applied across the pellet using copper electrodes, which is an increase of over 31 times.

A summary of the increase in the regression rate from the unpowered to the powered experiments can be seen in Table O.2, along with the minimum voltage required for the decomposition reactions to occur when copper is used as the electrode material. The unpowered regression rate of AN closely matched that of prior research (Young et al., 2013). Comparing the unpowered results to the applied 50 V case results in an increase in average regression rate of 30–58 times.

Table O.2: Summary of voltage experiments

Sample	Weight Percentage of Components	Unpowered Average Regression Rate (mm/s)	Average Regression Rate with 50 V (mm/s)	Minimum Voltage for Reaction to Occur (V)
SO1	100% AN	0.045	1.41	20
SO2	100% LP	0.017	0.99	30
SO3	50% LP/50% AP	0.020	1.13	40
SO4	20% LP/80% AP	0.037	1.16	40

For all the experiments carried out in addition to measuring the applied voltage, the current draw was also collected to develop an understanding of the relationship between regression rate and current draw. Figure O.9 shows regression rates for all the trends for each of the solid oxidizers under consideration as a function of current draw with the copper electrodes. For SO1 and SO2, it can be clearly seen that as the current increases the regression rate increases. SO3 and SO4 do not show as strong of a relationship between the current and the regression rate. Generally, the trends do show an increase in regression rate with current; however, there is still a significant amount of scatter that can be attributed to inconsistent contact between the melt layer and electrodes. Using the current draw and applied voltage at each data point, the power can be calculated and plotted versus the regression rate, as shown in Fig. O.10. In doing so, the trends clearly show an increase in regression rate with increasing power, which is also accompanied by a reduction in scatter in comparison to the trends with voltage and current. This is due to the fact that the magnitude of the applied voltage and contact strength of the electrodes with the melt layer, associated with the current, are coupled.

From Figs. O.9 and O.10, it is clear that SO4 (80% AP/20% LP) draws very little current and therefore does not require much power to obtain high regression rates. Regardless of how much voltage was applied across SO4, the current draw did not change substantially. SO3 (50% AP/50% LP) drew more current than SO4, likely due to the slightly larger melt layer resulting from the higher LP concentration. SO3 exhibited large data scatter in the regression rate value at a given current and power, as shown in Figs. O.9 and O.10. This was believed to be due to the melt layer being partially ejected and reformed rapidly over the course of the applied voltage. As a result, there was a change in the melt layer thickness and contact area with the

electrodes, which caused a high amount of variation in the current draw at a given moment. The current measurements in SO2 (100% LP) follow the most linear trend, likely due to this sample appearing to keep in contact the best with the electrodes compared to all of the other samples tested. However, even with the strong contact with the electrodes in SO2, the regression rate per current and power input was still low compared to the other samples. SO1 (100% AN) had a moderate amount of spread in the current to regression rate and the power to regression rate plots due to the amount of gas bubbles that form inside of the melt layer and at the interface of the melt layer and electrodes. This caused the contact between the liquid layer and the electrodes to fluctuate greatly over the course of the experiment.

The average resistance of each of the samples during the applied power experiments along with the resistance of the solid phase are listed in Table O.3. Comparing the solid phase resistance to the melt layer resistance, the solid phase has an average resistance over eight orders of magnitude larger than the melt phase. The large resistance in the solid phase was expected and confirms the findings by Khoruzhii, which stated that the solid phase of the oxidizers was nonconductive

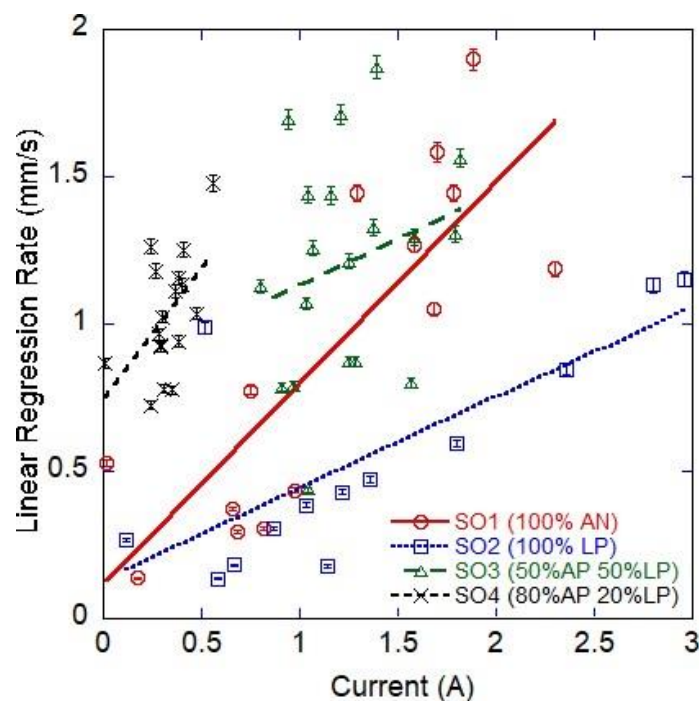


Fig. O.9: Current draw vs. regression rate

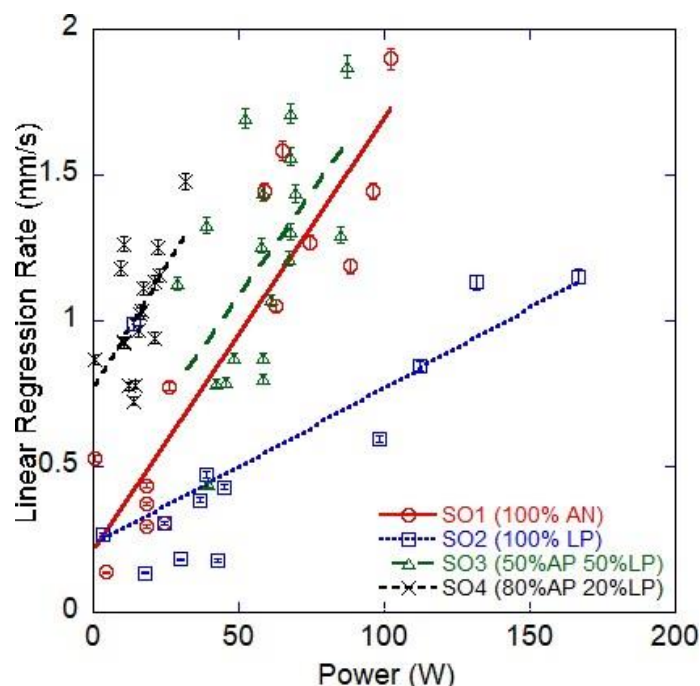


Fig. O.10: Total power vs. regression rate

Table O.3: Solid oxidizer resistance

Sample	Weight Percentages of Components	Solid Phase Average Resistance (Ohms)	Melt Layer Average Resistance (Ohms)
SO1	100% AN	5.02E+11	31
SO2	100% LP	2.23E+10	34
SO3	50% LP/50% AP	5.49E+10	42
SO4	20% LP/80% AP	1.62E+11	144

(Khoruzhii et al., 2007, 2008). The melt layer resistance of SO1, SO2, and SO3 are all close in magnitude, which verifies the current draw values seen in Fig. O.9 where these three compositions draw similar current. SO4 has a melt layer resistance that is four times that of the other oxidizer compositions. This higher resistance explains why the current draw of SO4 shown in Fig. O.9 is substantially lower, relative to SO1, SO2, and SO3.

In addition to exploring the increase in the regression rate of the solid oxidizers under a steady applied power, power cycling was explored to see if the reaction could start, stop, and restart just by turning on and off the power supply. SO4 (80% AP/20% LP) was selected for this experiment since the other solid samples had larger melt layers that would often spill off and solidify once the power was turned off. Spillage of the melt layer prevented the solid oxidizer pellet from moving freely in the experimental apparatus. As seen in Fig. O.11, the power supply was turned on at 11 s, and then at about 17 s the current draw increased while the displacement of the sample changed rapidly. The observed delay was caused by a melt layer that was not fully formed. If the melt layer was not fully formed, connecting the electrodes when the power supply

was turned on, time was required to allow the melt layer to grow, completing the circuit. Once the melt layer grows from one electrode and connects with the other, the circuit is completed, current can flow, and a sharp increase in the decomposition rate takes place. Once the power was turned off at 18 s, corresponding to a sharp drop in voltage, the current draw dropped, and the displacement of the pellet leveled out, showing that the reaction ceased. The power was then turned back on at 20 s, as shown by the sharp increase in the voltage. After a short pause, the reaction was reinitiated, as shown by the increase in the current draw, which resulted in a sharp increase in the displacement change after another short delay. This process was repeated with several samples of the SO4 composition, and a similar trend was observed. The biggest factor that dictated whether the reaction could restart was if there was still any liquid melt layer present. The conductive liquid melt layer was necessary to allow the reaction to take place. If the melt layer was not completely solidified in between power applications, the decomposition could be restarted reliably.

O.2.3 Effect of Electrode Material on Regression Rate

As seen in Figs. O.6 and O.7, there was a clear reaction taking place between the copper electrodes and the solid oxidizers. In order to determine the role that copper was playing in the increase in the decomposition of the solid oxidizers, experiments were conducted using platinum electrodes for SO1 (100% AN) and SO2 (100% LP). When considering the power input to the solid oxidizer versus the corresponding regression rate, as seen in Fig. O.12, there was a slight change observed for each of the electrode materials. In the case of AN, the use of platinum electrodes seemed to cause a slight decrease in the regression rate when compared to the copper electrodes. This is likely due to the exothermic reactions that take place in the reaction of Cu^{2+} with the various decomposition products of AN, which would accelerate the overall decomposition.

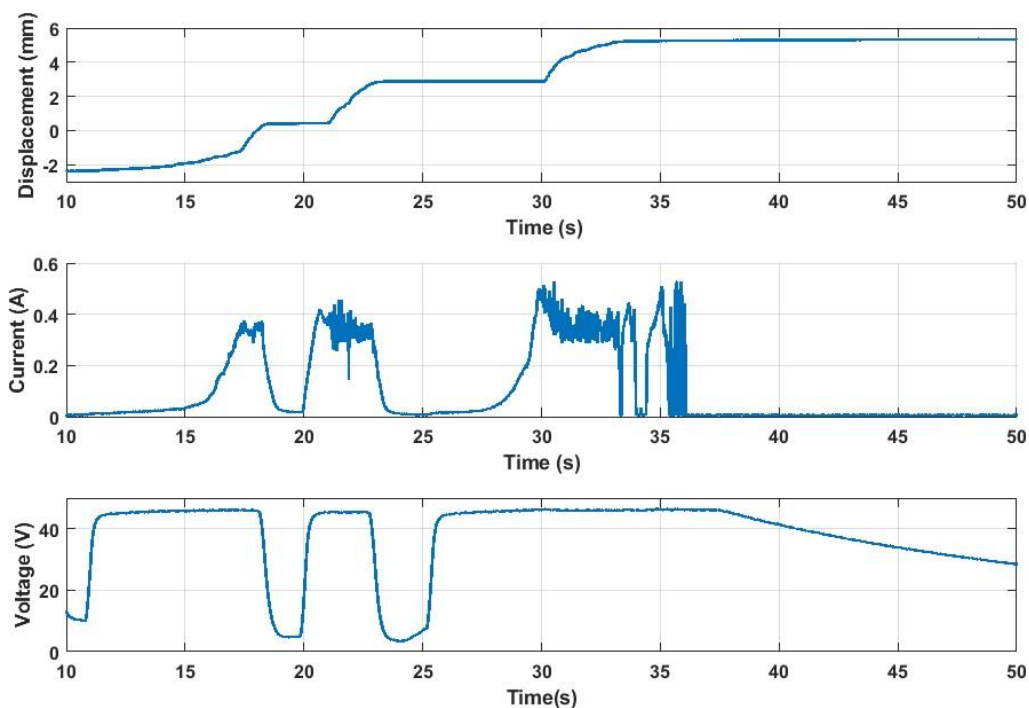


Fig. O.11: Regression rate with power cycling on 80% AP 20% LP sample

The effect the platinum electrodes have on the LP regression rate was much stronger, with the platinum electrodes resulting in a higher regression rate compared to the copper electrodes. This was not expected due to copper oxide being a strong catalyst in perchlorate decompositions (Qin et al., 2014; Zhang et al., 1996; Chen et al., 2008). The hypothesized cause for the lower regression rate when the copper electrodes are used is the nonconductive nature of the copper oxide that is formed directly on the copper wire, causing passivation effects (Anders and Plambeck, 1968). Due to copper oxide being significantly less conductive than pure copper, less energy is transmitted into the liquid melt layer, therefore lowering the effectiveness of the electrochemical reaction. This phenomenon was not observed with the AN samples, as Cu^{2+} , which was formed in the melt layer, remains soluble. As a result, the conductivity of the copper electrode is not impacted as greatly with AN. With LP, the electrochemical reaction may be inhibited as the copper electrode conductivity is reduced.

O.3 Conclusion

An experimental study was carried out to analyze the effect of an electrical stimuli on the regression rate of solid oxidizers composed of ammonium nitrate (AN), lithium perchlorate (LP), and ammonium perchlorate (AP) at atmospheric conditions. The use of AN and LP resulted in large conductive melt layers that were required for the electrical stimuli to accelerate the regression rate. The application of electrical power to the melt layer resulted in a sharp increase in the gaseous decomposition products observed forming in the melt layer, which corresponded to the increase in the regression rate. This increase in regression rate is due to the electrochemical decomposition of the oxidizers overcoming the rate-limiting steps present in thermal decomposition. For the case of pure AN, the application of 50 V DC resulted in a regression rate 31 times that of AN burning with 60 mL/min of ethylene gas. AN also was found to strongly interact with copper electrodes, which resulted in Cu^{2+} and helped to catalyze the decomposition reaction. A similar trend was observed with LP, where an increase in the linear regression rate of 58 times was found when 50 V DC was applied compared to LP burning with 60 mL/min of ethylene gas. LP also strongly interacted with the copper electrodes, resulting in copper oxide. Adding AP into the blend with LP at mass ratios of 50% LP/50% AP and 20% LP/80% AP and applying 50 V DC resulted in an increase in regression rates of 57 and 31 times that of burning with gas alone, respectively. The ability to start, stop, and restart the decomposition of all tested solid oxidizer samples was observed through the use of an applied voltage alone. As long as the melt layer does not completely solidify, therefore becoming nonconductive, reapplying the voltage restarts the decomposition reaction. The drastic increase in the regression rate through the use of an applied voltage, along with the ability to start, stop, and restart the decomposition of solid oxidizers, shows great promise in the potential of electrically controlled propulsion.

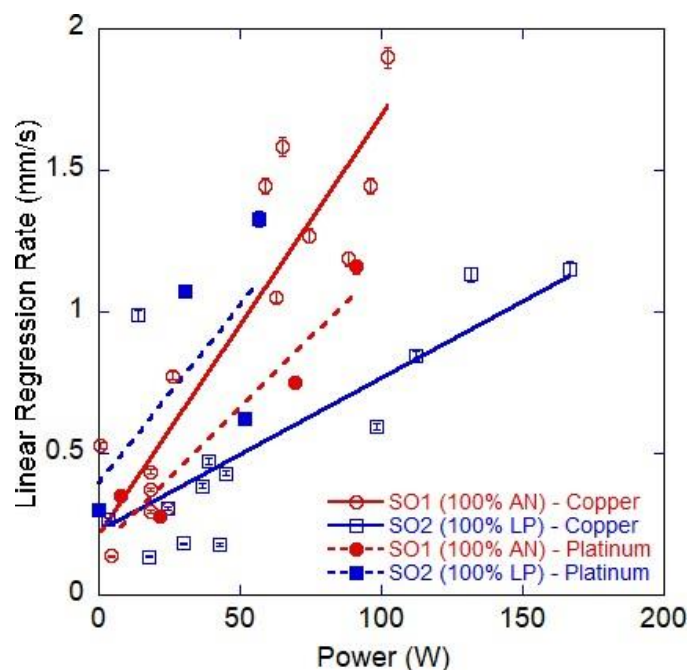


Fig. O.12: Regression rate vs. power for different electrode materials

Gel Study 1 “G1”

The goal of the research outlined in this paper was to explore the response of GPE based ECGPs when subjected to an applied electrical power at various magnitudes. ECGPs can be utilized to provide the ability to manipulate the decomposition and combustion rate during operation. The composition of the ECGPs was changed in order to determine the effects of composition on the response time, conductivity, and material properties. The gel ionically conductive polymer considered in this study was PEG and the oxidizing ionic salts used were lithium perchlorate (LP) and ammonium perchlorate (AP). The electrochemical decomposition process of the ECGPs was the main focus of our study in order to provide a greater understanding into the mechanisms that enable the decomposition to occur at an accelerated rate when compared to standard thermal means.

G1.1 Methods

G1.1.1 Sample Preparation

The ECGPs were created by placing a beaker with acetonitrile, which was purchased from Fisher Scientific and had a purity of 99.9%, on a stir plate and adding in the desired amount of oxidizer. The oxidizers used in this study were 200 μm LP and AP, both of which were purchased from Firefox Enterprises and had a stated purity of over 99.0%. The oxidizers were selected as they both could be complexed with PEG (Gray, 1991) and are strong oxidizers. The beaker was covered with a lid and allowed to stir for 6 hrs. Next, the necessary amount of polyethylene glycol (PEG) 400, which was purchased from Sigma Aldrich, was added to the solution, recovered with the lid, and allowed to stir for an additional 24 hrs. Next, the lid was removed from the beaker to allow the solvent to escape and stirred until the solution became too thick to stir with

the stir plate. Finally, the solution was placed in a vacuum oven for 24 hrs to remove any remaining solvent or absorbed water.

From a performance perspective, the specific impulse increases with increasing AP content versus LP content. However, increasing LP versus AP content is expected to improve ion conductivity, which may result in improved response time. Initial screening experiments with 100% AP and 75% AP (oxidizer balance LP) did not extinguish with the removal of applied power. Thus, a compromise of a 50/50 blend of AP and LP was selected for study. All mixtures studied were fuel rich. To determine a starting point for the fuel to oxidizer ratio of the ECGPs the NASA CEA program (Gordon, 1994) was utilized and the specific impulse and flame temperature was calculated for a range of PEG to oxidizer ratios as shown in Fig. G1.1. The oxidizer mixture was a 50/50 blend of AP and LP by weight and the CEA program was set up in the rocket problem solver with a chamber pressure of 6.8atm, an exit expansion ratio of 100, and equilibrium composition properties. The specific impulse and flame temperature of hydrazine is provided as a reference as it is a commonly used monopropellant (Hasan, 2019). The calculations indicate that the peak theoretical flame temperature and specific impulse occur with about 20% polymer. However, this mixture proved to be too viscous to be easily extruded. The percent polymer was increased until ECGPs were created that had a low enough viscosity that they could be utilized in our combustion experiments, which will be detailed in Section G1.1.5. The mass percentage of the PEG and oxidizer salts of the ECGP solutions considered in this study are listed in Table G1.1, and are shown relative to the theoretical flame temperature and specific impulse in Fig. G1.1. Despite not being able to use the ECGP composition with the peak theoretical thermochemical properties, all the compositions used in this study have higher specific impulses and flame temperature than hydrazine, which is generally undesirable for catalyst survival in monopropellant systems.

Table G1.1. ECGP Composition

Sample Name	Percent Polymer	Percent LP	Percent AP
ECGP1	27.0	36.5	36.5
ECGP2	33.3	33.3	33.3
ECGP3	39.6	30.2	30.2

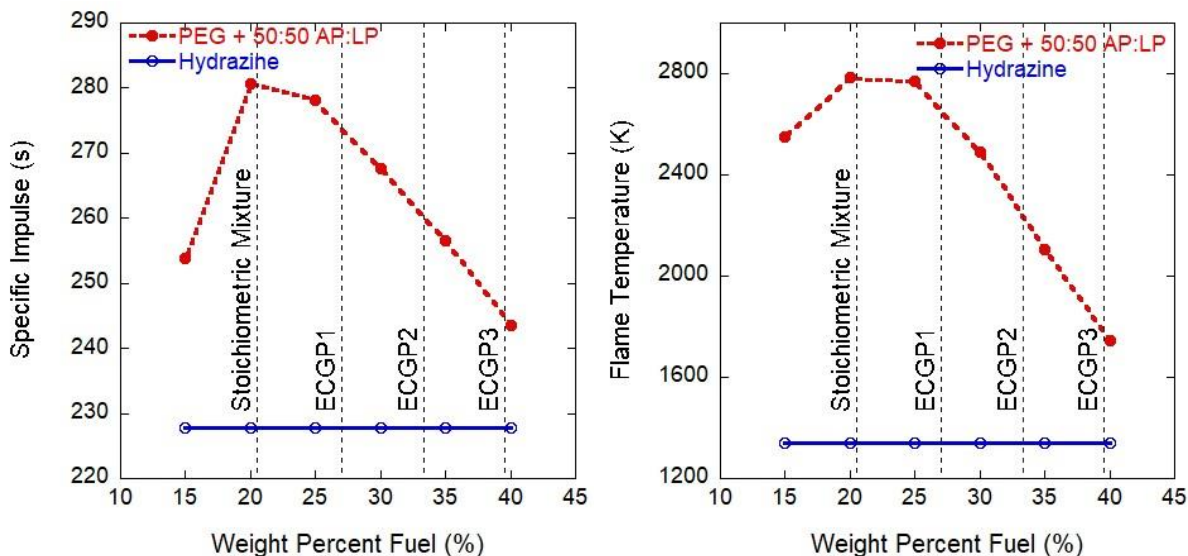


Fig. G1.1 Flame Temperature and Specific Impulse of PEG Based ECGPs

G1.1.2 Rheology Characterization

In order to understand the flow and deformation properties of the ECGPs that were created, a rheological study was performed. These experiments were conducted using a TA Instruments Discovery HR30 Rheometer, which was in a parallel plate configuration using a 25 mm diameter sandblasted roughened plate and a separation distance of 1000 μm . The rheological properties of interest were the viscosity as a function of angular frequency for each ECGP composition. This provides insight into how the composition affects the ability to flow, or its ability to be pumped through a tube. Rheology properties were characterized over a range of temperatures ($20^\circ\text{C} > T > -20^\circ\text{C}$) since monopropellant systems are often used in satellite propulsion which must perform in cold conditions.

G1.1.3 Conductivity Measurements

Impedance spectroscopy was utilized to measure the ionic conductivity of the ECGPs, which demonstrates the compositional effects of the ECGPs when subjected to an applied voltage. A more conductive composition allows for a higher rate of ion movement, which can lead to quicker ignition. To carry out the impedance spectroscopy the desired sample was placed into a ceramic tube with graphite electrodes on either end. The graphite electrodes were then connected to an Autolab PGSTAT302N, which was used to conduct the impedance spectroscopy measurements. Impedance spectroscopy involves the application of a low magnitude AC voltage through a range of frequencies and measuring the resulting current response (Winie, 2020). The applied voltage and current response will have the same frequency but will be offset by an angle (θ) (Winie, 2020). At a given voltage frequency, the magnitude of the impedance (Z_o) can be calculated by using the magnitude of the applied voltage (v_o) and the current response (i_o) as defined by (Winie, 2020):

$$Z_o = \frac{v_o}{i_o} \quad (\text{G1.1})$$

The calculated impedance value can then be separated into its imaginary (Z'') and real (Z') parts defined as (Winie, 2020)

$$Z'' = Z_o \sin \theta \quad (G1.2)$$

$$Z' = Z_o \cos \theta \quad (G1.3)$$

Measuring and then plotting the real and imaginary impedance values over the entire range of AC frequencies gives the complex impedance plane plot, as shown in Fig. G1.2 for ECGP2. The nonzero intersect between the plot and the real Z' impedance axis gives the resistance for that sample (Winie, 2020).

G1.1.4 Thermal Decomposition Characteristics

It is believed ECGPs used in this study initially decompose due to electrochemical means. However, once combustion is achieved, a combined thermochemical and electrochemical decomposition takes place. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were conducted on each ECGP composition to explore their response to thermal stimuli. The thermal decomposition analysis was conducted using a Netzsch STA 449 F5 Jupiter simultaneous thermal analyzer. The thermal analysis was conducted from 20°C to 650°C at a heating rate of 10°C/min in a nitrogen gas environment.

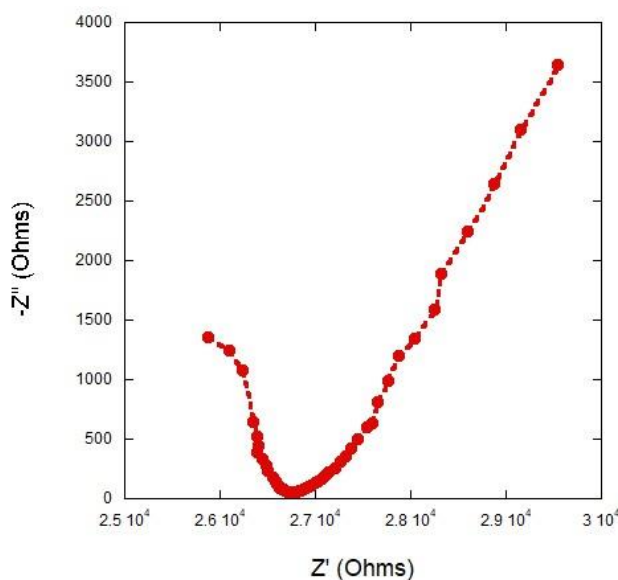


Fig. G1.2 Complex Impedance Plane Plot for ECGP2

G1.1.5 Combustion Experiments

To characterize the combustion characteristics of the ECGPs listed in Table G1.1, a series of experiments were conducted under a range of applied voltages (120V to 180V) and volumetric flow rates. To begin the experiments, the ECGP was loaded into a syringe which was loaded into a Harvard Apparatus PHD ULTRA syringe pump and a predetermined volumetric flow rate was set. The syringe was equipped with an electrically isolating ceramic tube, which was inserted into a ceramic base as shown in Fig. G1.3, which shows a bottom-up view of the experimental setup. The gel was pushed through the ceramic tube and into contact with the 6 mm tall by 65 mm long parallel copper plate electrodes, which initiated the decomposition and combustion reactions. The ceramic base contains the combustion reactions and a thin

slit allowed for pressure to be released during the experiment. The ceramic base and electrodes were then placed on a quartz plate as shown in Fig. G1.3, which shows a sideways cross-sectional view. The gel traveled along with quartz plate with the electrodes on either side. This entire configuration was elevated and held in place with a garolite stand. A mirror was placed under the quartz window, which enabled a Phantom VEO 7.10L high speed camera to safely record the decomposition and ignition process that occur as the ECGP reacts as shown in Fig. G1.4.

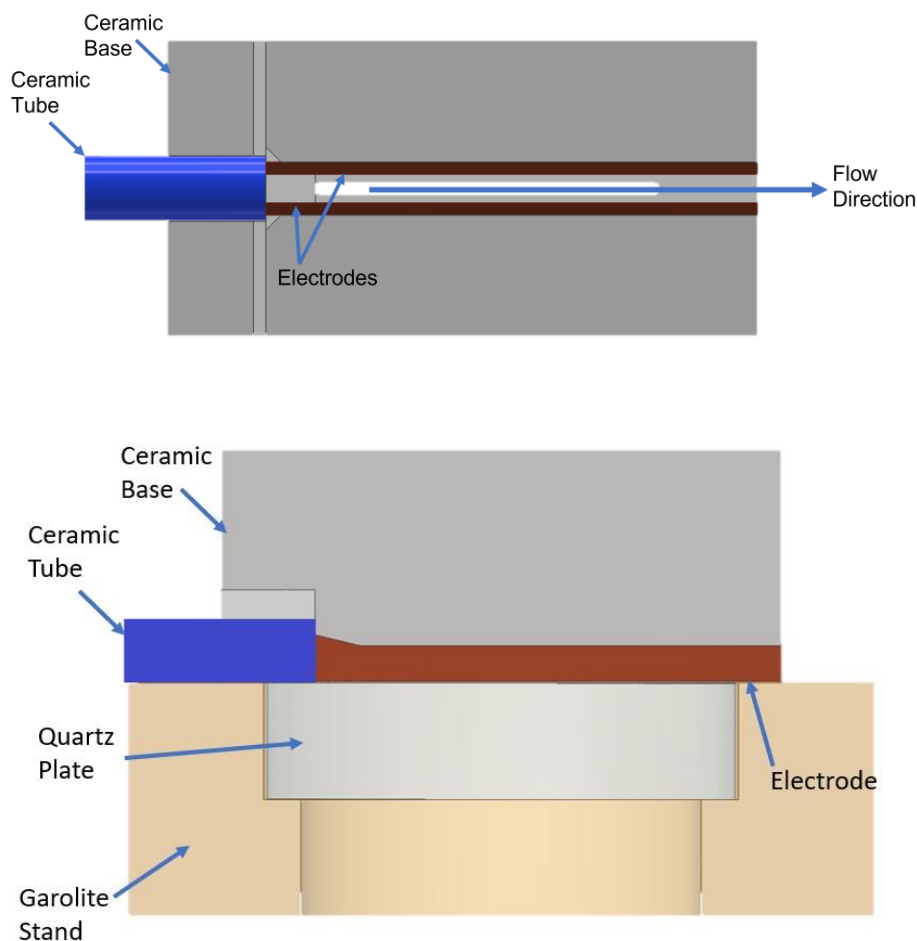


Fig. G1.3 Bottom Up View (Top) and Side Half Section View (Bottom) of Experimental Stand

Prior to the syringe pump being turned on, a predetermined voltage potential was applied to the electrodes using an XP Power HPT5K0-L DC power supply. The voltage was measured and recorded with a step-down circuit and a National Instruments SCB-68A data acquisition unit (DAQ). The current was also measured and recorded during the experiment with a Fluke i50s current probe and the DAQ. The use of high-speed cinematography enabled the determination of the location of ignition and the corresponding ignition delay. For this study, ignition is treated as first light observed in the recording. Using the location of the flame, the volumetric flow rate, and the cross-sectional area between the electrodes, the induction time was determined. The induction time of each ECGP was characterized for a set voltage to determine to compositional effects on the consumption rate and reaction time.

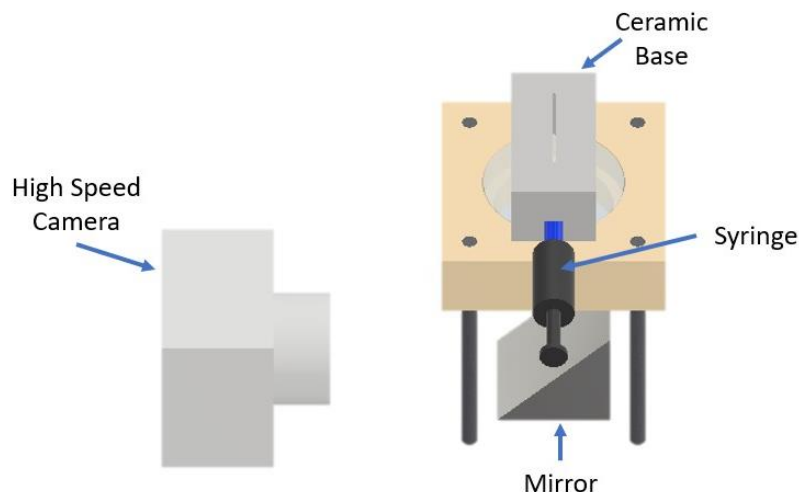


Fig. G1.4 Experimental Stand Assembly

G1.2 Results

G1.2.1 Rheology Characterization

The rheological properties of the ECGPs were found to be sensitive to the ECGP composition and temperature at which the rheometry was conducted. Figure G1.5 shows that ECGP1 has the highest overall viscosity, while ECGP3 has the overall lowest average viscosity. This illustrates the effect that the composition has on the rheological properties, with an increase in the liquid PEG polymer lowering the viscosity. As the temperature is decreased in the rheometry measurements, the viscosity increases for all of the ECGP compositions. As the concentration of PEG increases, the relative increase in the viscosity with decreasing temperature was observed to be greater compared to low PEG concentration ECGPs. In ECGP1, decreasing the temperature from 20°C to -20°C resulted in an order of magnitude increase in viscosity at low angular frequencies. For ECGP3, the increase in viscosity was around two orders of magnitude when decreasing the temperature from 20°C to -20°C. This demonstrates that while increasing the polymer concentration results in a composition with a lower overall viscosity, the higher polymer concentration causes a higher sensitivity to decreasing temperatures.

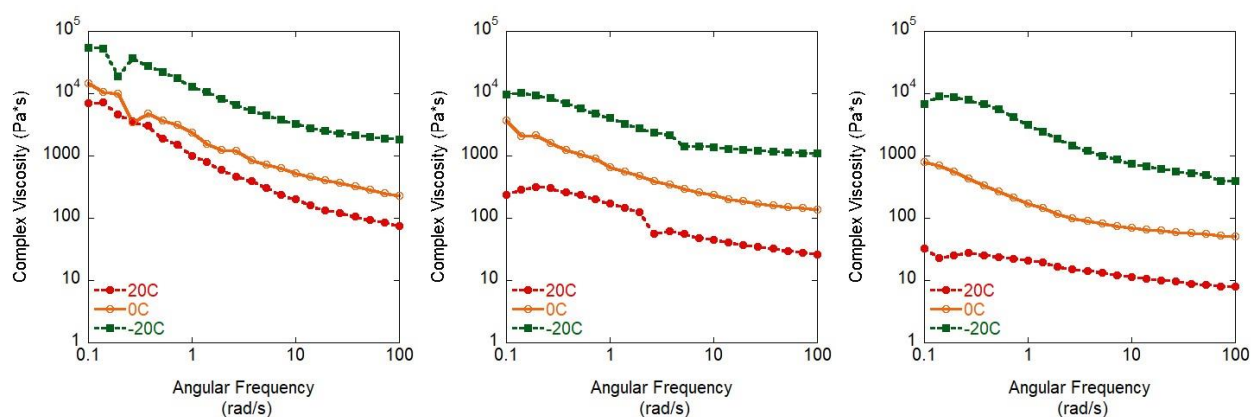


Fig. G1.5 Rheometric Properties of ECGP1 (Left), ECGP2 (Center), and ECGP3 (Right)

G1.2.2 ECGPs Conductivity

The impedance spectroscopy measurements conducted gave the resistance of each ECGP composition. However, the resistance value measured is dependent on the amount of sample used and the spacing between the electrodes. The measured resistance (R) was converted to resistivity (ρ) using the electrode contact area (A) and separation distance between the electrodes (L) by using Eqn. G1.4.

$$\rho = \frac{RA}{L} \quad (\text{G1.4})$$

Using three measurements per ECGP composition, the average and standard deviation of the resistivity for each ECGP composition was calculated and are shown in Table G1.2. The measurement error was calculated using the methods of (Kline, 1953), and is much lower than the statistical error. As such, the statistical error in the form of the standard deviation is reported. The resistivity did not vary significantly between ECGP1 and ECGP2, but ECGP3 was found to have a much lower resistivity. The inverse of resistivity is conductivity, thus a lower resistivity results in a higher conductivity. A higher conductivity indicates that ions can flow more readily through the ECGP, which may assist in the decomposition and combustion reaction.

Table G1.2 Resistivity of ECGP Compositions

Sample Name	Average Resistivity (Ωm)	Standard Deviation (Ωm)
ECGP1	477	42
ECGP2	484	15
ECGP3	124	17

G1.2.3 Thermal Decomposition

The results of the TGA and DSC analysis of the AP, LP and PEG are shown in Fig. G1.6 while results for the ECGP samples are shown in Fig. G1.7. ECGP1 and to a lesser degree ECGP2 show an endotherm occurring around 85°C which is likely the combination of evaporation of residual acetonitrile, which begins at 82°C (O'Donnell, 1965) and the endotherm associated with the LP used in this study that occurs at 87°C. The higher viscosity of ECGP1 and ECGP2 results in a higher concentration of residual acetonitrile being trapped in the sample when compared to ECGP3, so the contribution of this endotherm is more pronounced. Additionally, ECGP1 and ECGP2 have a higher concentration of LP compared to ECGP3, thus any endotherm associated with LP will be more prominent than in ECGP3. The endotherm observed at 240°C in every ECGP composition in Fig. G1.7 is the phase transformation of AP from orthorhombic to cubic (Kubota, 2016), which is also observed in the AP DSC curve in Fig. G1.6. The primary exothermic peak of the ECGPs were found to vary slightly with the changing composition with an increasing concentration of PEG resulting in the peak occurring at a higher temperature. This exothermic peak corresponds closely with the primary mass loss as shown in the TGA plot in Fig. G1.7, which indicates that this exothermic peak is likely caused by a thermal runaway. The exothermic peak of the ECGPs were measured between 284°C and 297°C, which closely matches the temperature of the exothermic peak of the AP as shown in

Fig. G1.6. LP has an exothermic peak occurring at 510°C as shown in Fig. G1.6, that is the result of the thermal decomposition of LP creating oxygen and lithium chloride (Markowitz, 1964), which was not observed in the DSC of the ECGPs. The final endotherm observed at 604°C can be attributed to the melting of LiCl (Kamali, 2011) which is formed from the thermal decomposition of LP (Manelis, 2003).

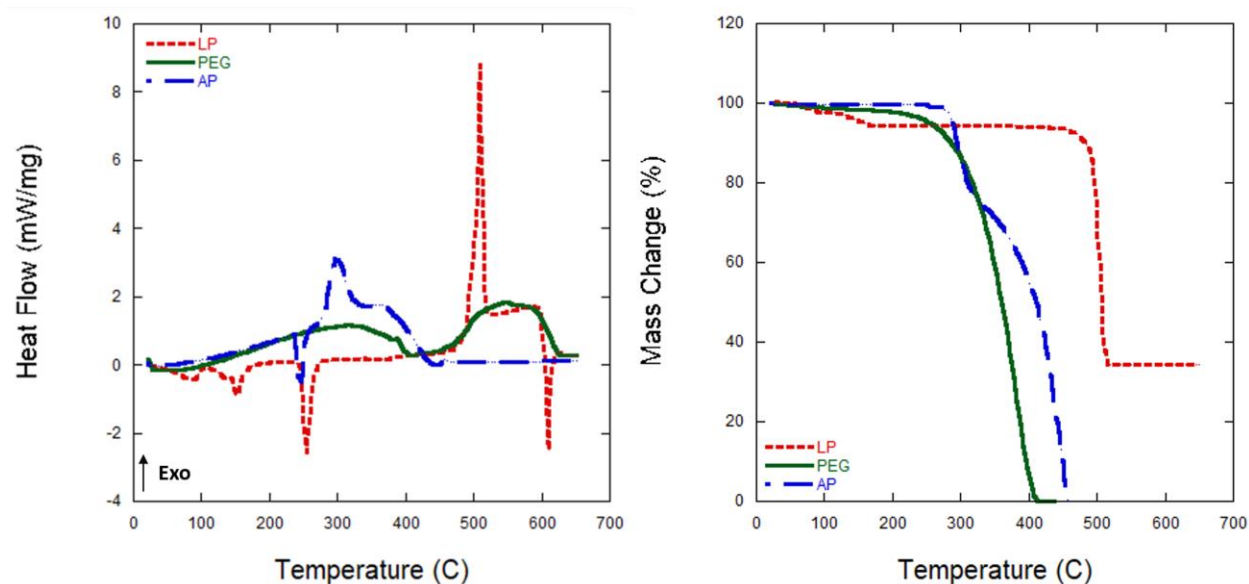


Fig. G1.6 Thermal Analysis Results of AP, LP, and PEG

G1.2.4 Combustion of ECGPs

When power was applied across the ECGPs, decomposition began followed by ignition after a short delay. The ignition delay depended on the magnitude of the voltage applied and the composition of the ECGP as shown in Fig. G1.8. Each of the points in Fig. G1.8 is the average of three experiments at a given applied voltage, with the error bars representing the standard deviation. The measurement error was calculated to be much lower than the statistical error. As such, the statistical error in the form of the standard deviation is reported. Ignition delay was determined using high-speed cinematography and taking the time between when the gels first make contact with the electrodes until first light is observed. For all of the compositions considered in this study, the ignition delay decreased as the voltage increased. All of the ECGP compositions examined in this study followed a linear decrease in ignition delay as the voltage increased. At 120V and 140V ECGP1 had the lowest ignition delay, but as the voltage increased ECGP2 and ECGP3 had the lowest overall ignition delay. ECGP2 had the overall longest ignition delay for all but the highest voltages, but it also displayed the greatest ignition delay sensitivity to applied voltage. This suggests that the ratio of polymer and oxidizer plays a vital role in the response time of the ECGPs. The composition ECGP3 has the lowest resistance as shown in Table G1.2 along with the lowest overall ignition delay on average. This suggests that having a higher conductivity, or ability for the ions to flow, tends to lead to a quicker ignition in the ECGPs.

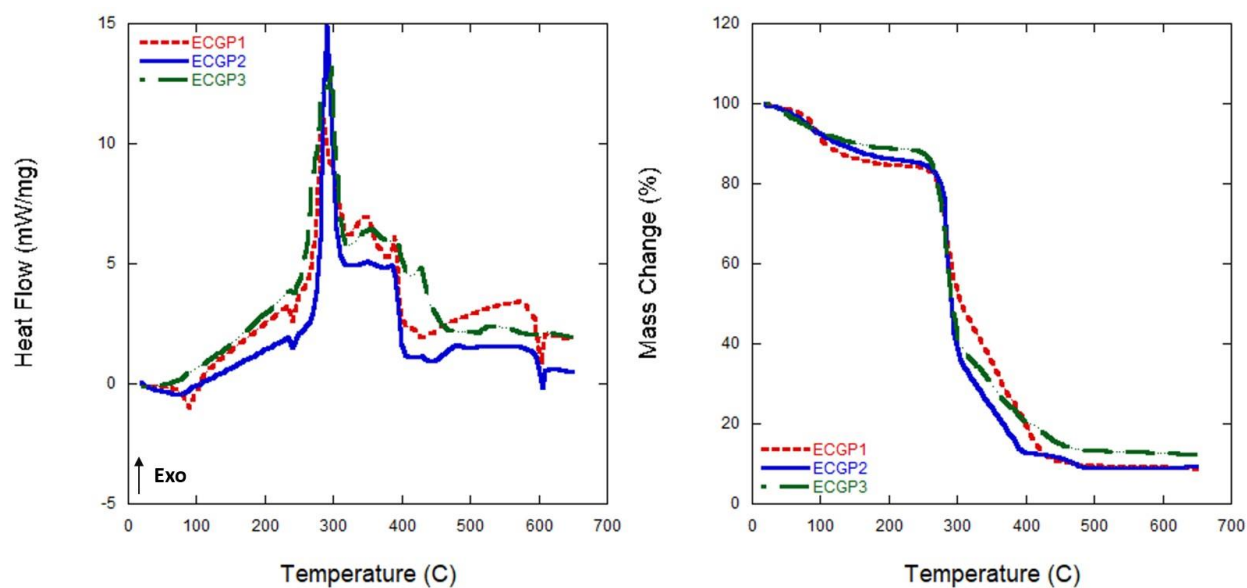


Fig. G1.7 Thermal Analysis Results of ECGP Compositions

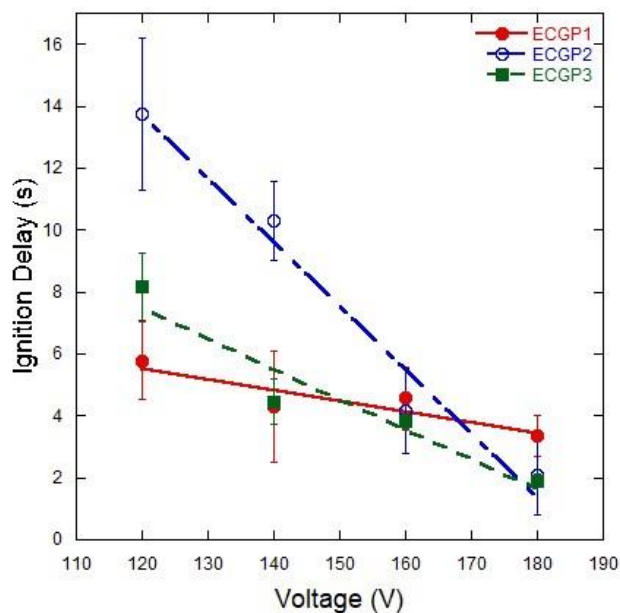


Fig. G1.8 Ignition Delay of ECGPs at Various Voltages

When lithium perchlorate is dissolved into an ionically conductive polymer like PEG, the anion and cation dissociate as shown in Eqn. G1.5 due to the interaction with the oxygen atoms in the PEG polymer backbone

(Watanabe, 1986). The oxygen atoms complex with the lithium cations from LP, and this complex enables the movement of ions when a voltage is applied. When the power is applied to the ECGPs, the lithium ions move towards the cathode, where they are reduced as shown in Eqn. G1.6 (Winie, 2020). Large anions such as perchlorates have a tendency to not move as freely through polymer electrolytes, however their movement cannot be neglected (Watanabe, 1986). The interaction of the perchlorate ions with the anode results in the perchlorate ions being oxidized, or losing an electron as shown in Eqn. G1.7 (Hashmi, 1999). The ECGP compositions are formed from solution. In our case, the solution has been saturated such that a small portion of the oxidizer could not be completely dissolved and complexed with the polymer. Therefore, a small quantity of undissolved oxidizer particles remains suspended in the final ECGP product. Once the decomposition and ignition reaction begins, and the excess undissolved oxidizer enters its molten phase, it is expected that the perchlorate ions will also electrochemically decompose as per Eqn. G1.8 (Anders, 1968).



Ammonium perchlorate behaves similarly to LP, by forming a complex with the PEG and dissociating into its anion and cation as shown in Eqn. G1.9 (Gray, 1991). The perchlorate anions in AP follow a similar path as shown in Eqn. G1.7 and Eqn. G1.8 for LP. The ammonium cation has two potential decompositions with the first being the reduction, or gain of electrons, of the ammonium ion at the cathode as shown in Eqn. G1.10 (Dong, 2016) and the second being a reduction of protons into hydrogen (Hashmi, 1990) as shown in Eqn. G1.11. The ammonium cation reduction reaction assumes that the whole ammonium ion can move and come into contact with the cathode. However, the ammonium ions also tend to create a proton (H^+) conducting mechanism where the weakly bonded hydrogen atoms in the ammonium ions hop between the coordinating sites in the ammonium ions (Hashmi, 1990). Hydrogen is then created by the reduction of these protons as per Eqn. G1.11 (Hashmi, 1990).



Images obtained using high-speed cinematography of the evolution of the decomposition process for ECGP3 are shown in Fig. G1.9. In Fig. G1.9 the time $t=0$ seconds corresponds to the time at which the ECGP comes into contact with the electrodes and is used as a reference time for the image sequence shown.

At time $t=0$ seconds, it can be seen that there is a clearly defined gel front that is traveling between the copper electrodes. The gel moves parallel to the electrodes as more material is extruded as shown at time $t=3.24$ seconds. At time $t=4.32$ seconds, decomposition of the ECGP begins to take place as shown by the large formation of gas, as evidenced by the formation of bubbles, at the end of the extruded gel. The amount of gas increases as time progresses in the decomposition reaction after which, a dark decomposition area begins to form as shown in Fig. G1.9 at time $t=4.51$ seconds. Ignition follows shortly thereafter at time $t=4.53$ seconds and occurred inside of the dark decomposition area for all ECGP combustion experiments conducted. Once ignition occurs, the flame grows and the flame front begins to move back towards the inlet as shown at time $t=7.10$ seconds. If the flow rate of the ECGP is sufficient, the flame front will reach a steady state where the location remains nearly constant.

To characterize the steady state burning characteristics of each ECGP composition, additional experiments were conducted to determine the required flow rate to match the consumption rate and the corresponding induction time. These experiments were conducted at 180V, and the propellant inlet flow rate was varied so that the location of the dark decomposition zone remained nearly constant. The flame front of the ECGPs is located in the center of the dark decomposition zone as shown in Fig. G1.9. By tracking the center of the dark decomposition zone, the combustion location was measured over the course of the experiment. An example of the results of tracking the dark decomposition area over the course of an experiment is shown in Fig. G1.10. The time $t=0$ seconds corresponds to the ignition of the ECGP, which was measured at around 17 mm from the point of first contact between the ECGP and the electrodes. Once the flame grows, it can be seen in Fig. 10 that the location of the decomposition zone moves towards the inlet, which is also shown in Fig. G1.9. The decomposition zone then reaches a nearly steady state point from time $t=3$ seconds until time $t=12$ seconds as shown in Fig. G1.10.

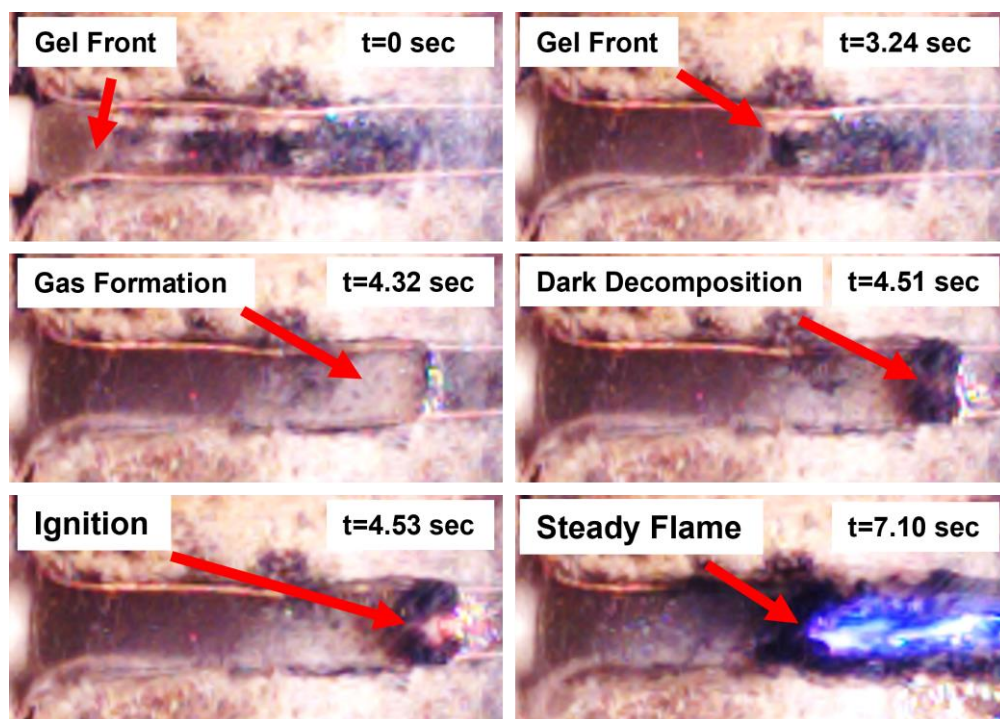


Fig. G1.9 Decomposition Evolution of ECGP3

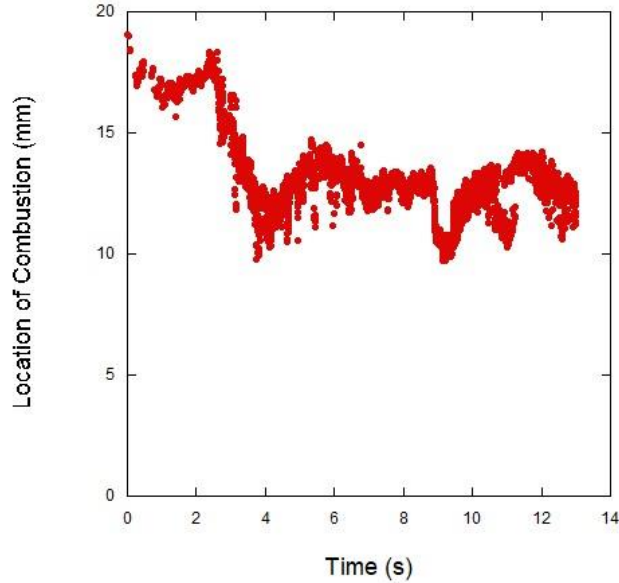


Fig. G1.10 Flame Front Over Time for ECGP3

Using the steady state location of the dark decomposition area, the steady state induction time can be calculated. The assumption is made that the cross-sectional area of the ECGP being extruded between the electrodes remains constant prior to and after extrusion. Using the known cross-sectional area (A_c) and volumetric flow rate ($\dot{v}$), the velocity of the flow (V) can be calculated as shown in Eqn. G1.12. Using the calculated velocity and the average steady state location of the dark decomposition area (x_f), the induction time (T_i) can be calculated using Eqn. G1.13.

$$V = \frac{\dot{v}}{A_c} \quad (\text{G1.12})$$

$$T_i = \frac{x_f}{V} \quad (\text{G1.13})$$

The required volumetric flow rate to maintain steady state combustion, the average steady state location of the decomposition area, and the average induction time from three experiments per ECGP composition is listed in Table G1.3. These results demonstrate that ECGP1 required the highest flow rate to maintain a steady combustion location and therefore had the lowest average induction time. The second lowest average induction time was ECGP3, with ECGP2 having a much higher induction time despite being a composition between ECGP1 and ECGP3. The proposed reason for this induction time trend is due to the electrochemical versus thermochemical properties of each composition. Comparing the peak flame temperature and specific impulse in Fig. G1.1 to the composition of the ECGPs in Table G1.1 shows that ECGP1 is the most thermally energetic composition. Therefore, while ECGP1 has the longest ignition delay of the compositions we explored at 180V, once ignition is achieved the high thermal energy allows it to combust at a higher rate with greater heat feedback from the flame zone into the incoming gel. Conversely, even though ECGP3 has the lowest thermal output of our compositions, the low induction time can be explained by the lower resistance of this composition. The low resistance allows for a higher rate of ions to flow and react, which leads to a quick ignition as shown in Fig. G1.8 and a high decomposition rate even though it is not a thermochemically ideal composition.

Table G1.3 ECGP Steady Burning Results at 180V

Sample Name	Flow Rate (ml/min)	Average Decomposition Location (mm)	Average Induction Time (s)
ECGP1	11	12.1	1.18
ECGP2	10	15.9	1.71
ECGP3	10	11.8	1.27

G1.3 Conclusion

An experimental study was conducted on ECGPs to determine how compositional changes affect the material properties and combustion characteristics. Changes in the amount of oxidizer salt and liquid PEG polymer were discovered to have a large effect on the rheological properties of the ECGPs. As the amount of liquid polymer increased, the ECGP had a lower overall viscosity across all temperature ranges considered in this study. Changing the ratio of polymer and oxidizer salt also had an effect on the conductivity of the ECGPs. The composition with the highest amount of polymer, ECGP3 had the lowest overall resistivity and therefore would allow ions to flow at the highest rate.

Changes in the composition of the ECGPs greatly affected the combustion characteristics such as the ignition delay and induction time for a steady-state combustion. Regardless of the composition, the ECGPs ignited substantially faster as the magnitude of the applied voltage was increased. It was determined that ECGP1 had the highest overall consumption rate and the lowest average induction time at 180V despite having the longest ignition delay at 180V. The long ignition delay can be explained by the high resistance of ECGP1, which inhibits the flow of ions that initiate decomposition. However, ECGP1 has a thermochemically favorable formulation compared to the other compositions, which enables a high consumption rate once ignition occurs. ECGP3 had the shortest ignition delay, which can be attributed to its low resistance and therefore higher rate of ion flow. The lower resistance also enables ECGP3 to have the second fastest induction time as shown in Table 3. These results indicate that the electrochemical and thermochemical decomposition of the ECGPs both play a role in the combustion reactions taking place and are affected by the composition of the ECGP used.

Gel Study 2 “G2”

The following investigation focused on continuing the work completed by Gobin et al. with the development and characterization of fundamental properties of electrically controllable gel polymer electrolyte monopropellants (Gobin, 2022). Experiments were completed to characterize the ignition/combustion, mechanical, electrochemical, and thermal properties of five ECGPs as a function of the ratio of the propellant’s oxidizer salts. Ignition/combustion aspects were investigated by observing ignition characteristics as a voltage potential is applied to the propellants, followed by a study completed with select propellants under varying pressures to describe its burn and extinction properties. Their mechanical and electrochemical properties were determined through rheological measurements and electrical impedance spectroscopy (EIS) studies, respectively, and the thermal characterization study was conducted to understand the thermal decomposition of the propellant constituents.

G2.1 Methodology

G2.1.1 Sample Preparation

The polymer used in this study was $400\text{g}\cdot\text{mol}^{-1}$ molecular weight polyethylene glycol (PEG) sourced from Sigma-Aldrich, with oxidizer salts of ACS grade lithium perchlorate (LP), sourced from Thermo Fisher Scientific with a minimum 95% purity, and ammonium perchlorate (AP) with a stated particle size of 200 microns from Pyro Chem Source. Lithium perchlorate was selected as the primary oxidizer alongside the PEG due to the extensive research available on these components in GPE applications (Xue, 2015; Li, 2017; Mao, 2001). The monopropellants were prepared by dissolving the polymer in acetonitrile, which was sourced from Thermo Fisher Scientific with a minimum purity of 99.9%, and subsequently adding the oxidizer salts. The mixtures were stirred over heat while covered until the oxidizer salts were sufficiently dissolved and then stirred uncovered to allow the solvent to evaporate and the mixtures to thicken. In the propellants that were supplemented with AP, it was observed that the larger AP particles do not fully dissolve, however, and are instead suspended in the gel matrix. The mixtures were further dried in a vacuum chamber, where they remained stored until experimentation to ensure no atmospheric moisture was absorbed.

The study was constrained by the burn characteristics of AP, for which controllability became a concern. An examination of an early propellant, which had an oxidizer composition of 50% AP and 50% LP as well as polymer to oxidizer ratio of 1:3, resulted in a self-sustained flame, demonstrating that this would be an upper limit of AP present in the propellant. Thus, data collection began with a baseline propellant that utilized only LP as its oxidizer, and following iterations saw the incremental addition of AP. Theoretical values of flame temperature and specific impulse were calculated using NASA's Chemical Equilibrium with Applications program (CEA) (Gordon, 1994). The CEA program was used to find the peak for these values as a function of weight percent polymer in a PEG and LP propellant as well as a PEG and AP propellant using the equilibrium rocket problem with an assigned chamber pressure of 0.689 MPa and a supersonic area ratio of 100. The results of the calculations can be found in Fig. G2.1 and G2.2 below, which show that both the flame temperature and vacuum specific impulse peak at 25% polymer mass for the LP and PEG composition, while this occurs for 15% polymer mass for the AP and PEG composition. Because of the focus of this research on the use of LP as the primary oxidizer, investigations proceeded with monopropellant candidates with a polymer content of 25% by mass. Figure 2 depicts the flame temperature and vacuum specific impulse for a propellant composed of LP and PEG fixed at the selected polymer-to-oxidizer ratio as a function of increasing percent AP of the total oxidizer mass. Vertical black dashes on each represent the composition of the propellant candidates and are labeled as such, and Table G2.1 further details these candidates.

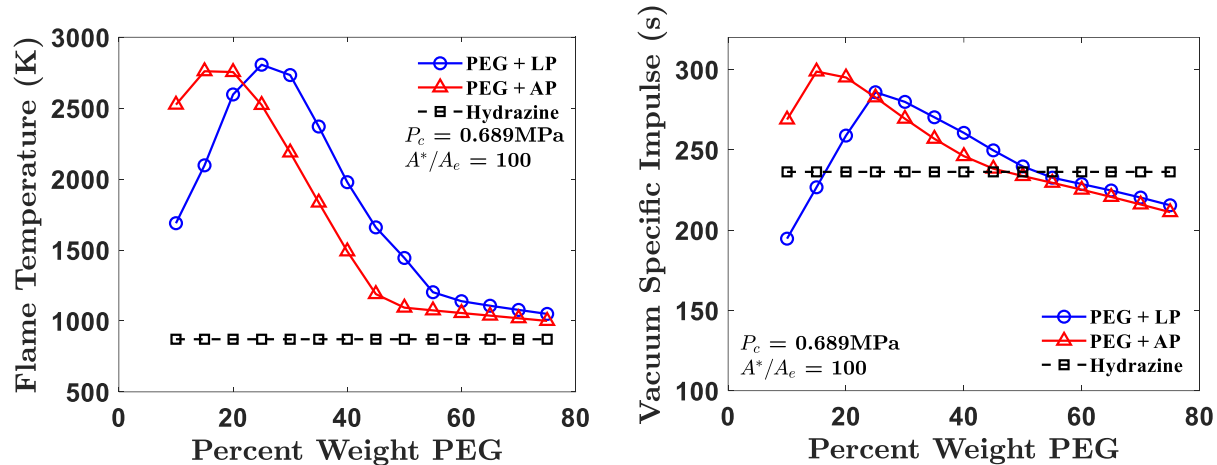


Figure G2.1 Polymer weight percent vs. flame temperature (top) and vacuum specific (bottom) impulse for PEG+LP and PEG+AP compositions.

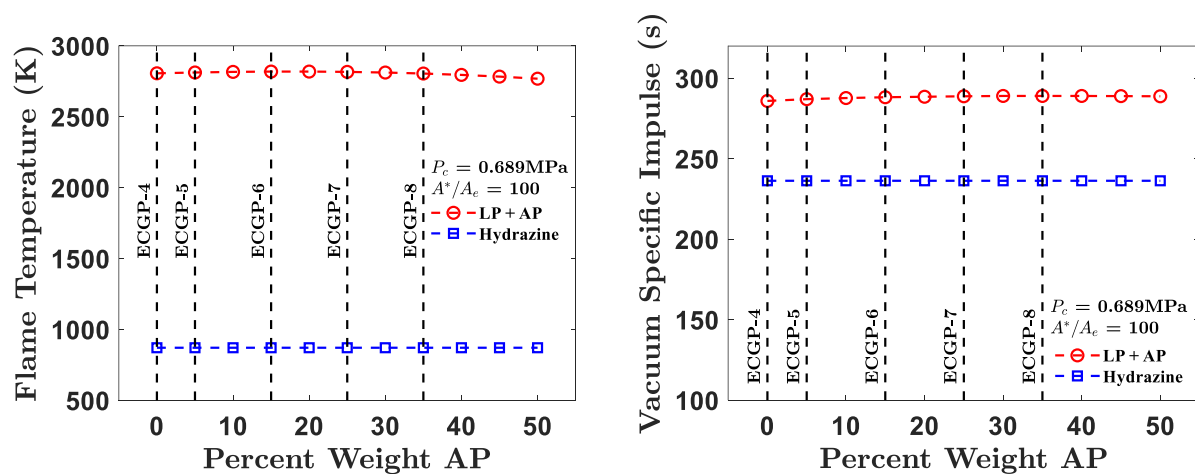


Figure G2.2. AP weight percent of total oxidizer vs. flame temperature (left) and specific impulse (right) at 25% weight polymer.

Table G2.1. Compositions of gel propellant candidates.

Candidate Name	%wt PEG	%wt LP	%wt AP
ECGP-4	25.00	75.00	0.00
ECGP-5	25.00	71.25	3.75
ECGP-6	25.00	63.75	11.25
ECGP-7	25.00	56.25	18.75
ECGP-8	25.00	48.75	26.25

G2.1.2 Ignition Characteristics

Experiments completed to characterize electrolytic ignition aspects consisted of extruding the monopropellants into the channel of a ceramic block where they come into contact with parallel copper electrodes running the length of the block. A voltage was supplied to these electrodes via an XP HPT5K0- L DC power supply. This was done for a ceramic block with electrode gap widths of 0.635 cm for all propellant compositions as well as 0.318 cm for ECGP-4 to investigate ignition dependence on both applied voltage and electrode spacing. The propellants were fed into the ceramic block via a syringe that was loaded into a Harvard Apparatus PHD Ultra syringe pump. The syringe was outfitted with a ceramic tube at its exit to ensure the syringe pump was electrically isolated from the electrodes. This assembly was placed on top of a quartz window with a mirror situated underneath for a Vision Research Phantom VEO 7.10L high-speed camera to capture video. This experimental set up is visualized in Fig. G2.3, as detailed by Gobin, et. al. (Gobin, 2022). With a sufficient voltage applied to the electrodes, the gel begins to decompose and finally ignite. Ignition delay was characterized over a voltage range of 120V to 180V in increments of 20V. The ignition delay was defined as the time between a gel's first contact with the electrodes and first light. With knowledge of the respective frames of these events and the sample frame rate of the camera, the ignition delay can be determined.

Additional static experiments were carried out in which a gel sample was placed between two electrodes while being monitored by a Telops FAST M3K high-speed infrared camera to capture the in-situ thermographs of the samples during the electrochemical reactions. A G4x microscope lens from Telops with a resolution of approximately 10 microns per pixel was used in this study. Residue collected from this experiment, along with the starting material, were analyzed using ATR-FTIR on a Nicolet iS50R spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The spectra were collected at a resolution of 4 cm⁻¹, and each spectrum consisted of 40 scans that were averaged every 60 seconds. The data was processed using Happ-Genzel apodization, Mertz phase correction, and atmospheric suppression techniques.

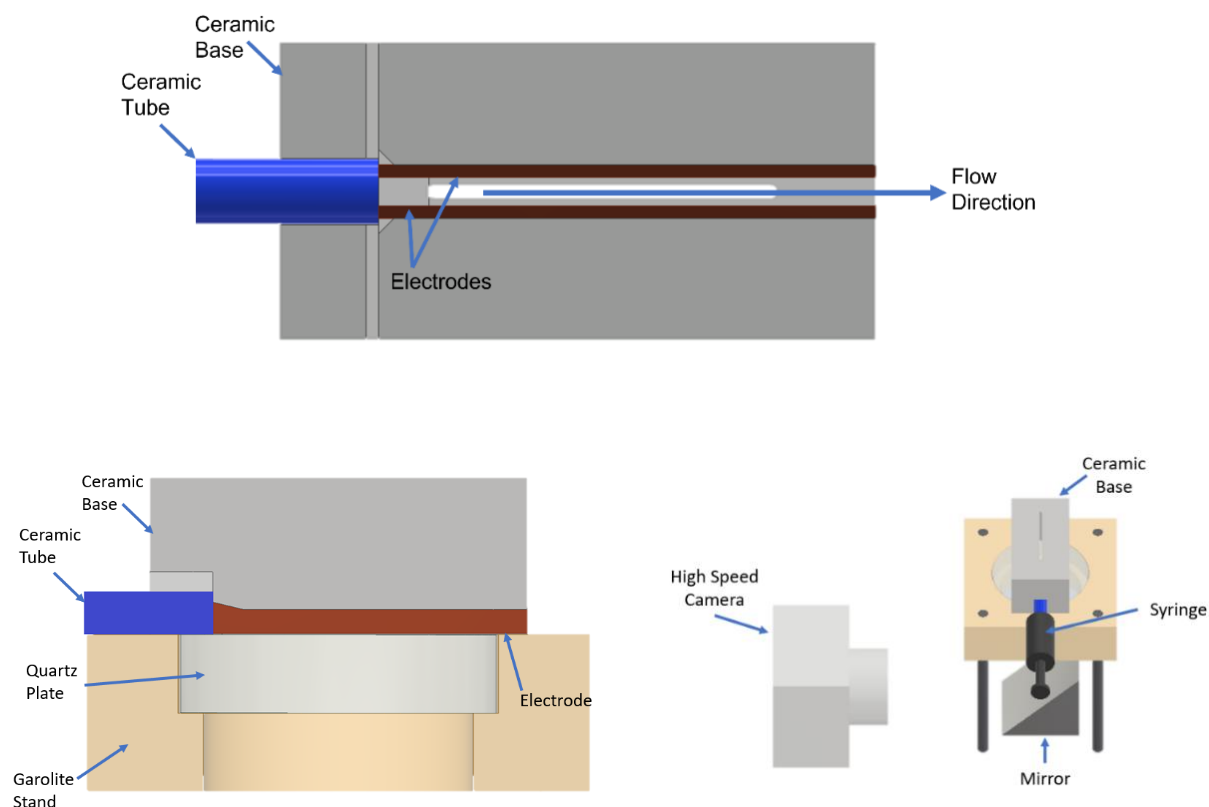


Figure G2.3. Detailed apparatus set up (Gobin, 2022), depicting bottom-up view (top), side-half-section view (left), and the experimental stand assembly (right).

G2.1.3 Pressure Study

ECGP-4, ECGP-6, and ECGP-8 were selected to be studied under pressure in an optically accessible strand burner with a nitrogen purge to determine their pressure deflagration limit (PDL) and the corresponding burn rate. The propellants were placed in a sample carrier composed of a quartz tube with one end open and the other sealed by a 3D printed cap. A nichrome ignition wire was placed in contact with an igniter propellant, which rested on top of the propellant sample at the open end of the tube. The igniter was an AP composite solid propellant made in house and was composed of 65% by mass AP with a stated particle size of 200 microns, 10% AP with a stated particle size of 90 microns, both sourced from Pyro Chem Source; 17% hydroxyl-terminated polybutadiene (HTPB), with R-45 polymer and methylene diphenyl diisocyanate (MDI) curative sourced from RCS Rocket Motor Components, inc.; and 8% H₂ spherical aluminum powder sourced from Valimet, inc. with a minimum purity of 99.7% and a particle size between two and three microns, per the supplier. The tube assembly was held in the strand burner by a flame-retardant fiberglass-epoxy composite base. The configuration is visually detailed in Fig. G2.4 below. The pressure deflagration limit and respective burn rate of ECGP-4, ECGP-6, and ECGP-8 were found as a result of this study.

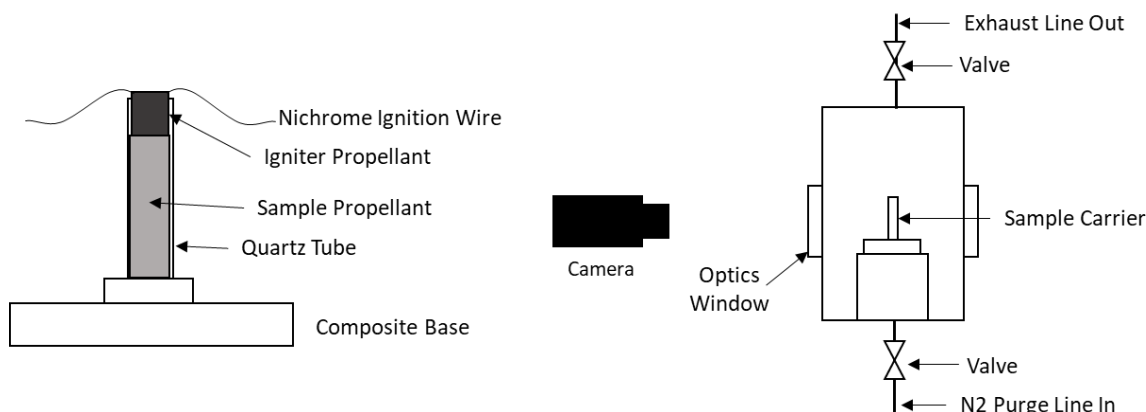


Figure G2.4. Detailed view of strand burner sample carrier (left) and strand burner experimental set up (right).

G2.2. Material Characterization

G2.2.1 Rheological Characterization

A rheological study is necessary for all liquid and gel propellants to help understand their pumping requirements at expected operating temperatures. This was completed to observe the impact of varying oxidizer content on the flow properties of the ECGPs. Using a Discover HR-30 Rheometer with a 25mm sandblasted parallel plate and a separation distance of 1000 microns, each propellant was subjected to rotational oscillations at angular frequencies ranging from 0.1 to 100 $\text{rad}\cdot\text{s}^{-1}$ and temperatures ranging from -20°C to 20°C .

Results of the rheology study can be found in Fig. G2.5. For all ECGPs, viscosity increases with decreasing temperature. The gels displayed a thixotropic behavior as their viscosity decreased with increasing applied angular velocity. At -20°C , it is shown that increasing AP content decreases the viscosity of the gels. This may in part be due to the replacement of dissolved LP with the suspension of partially dissolved AP particles in the matrix.

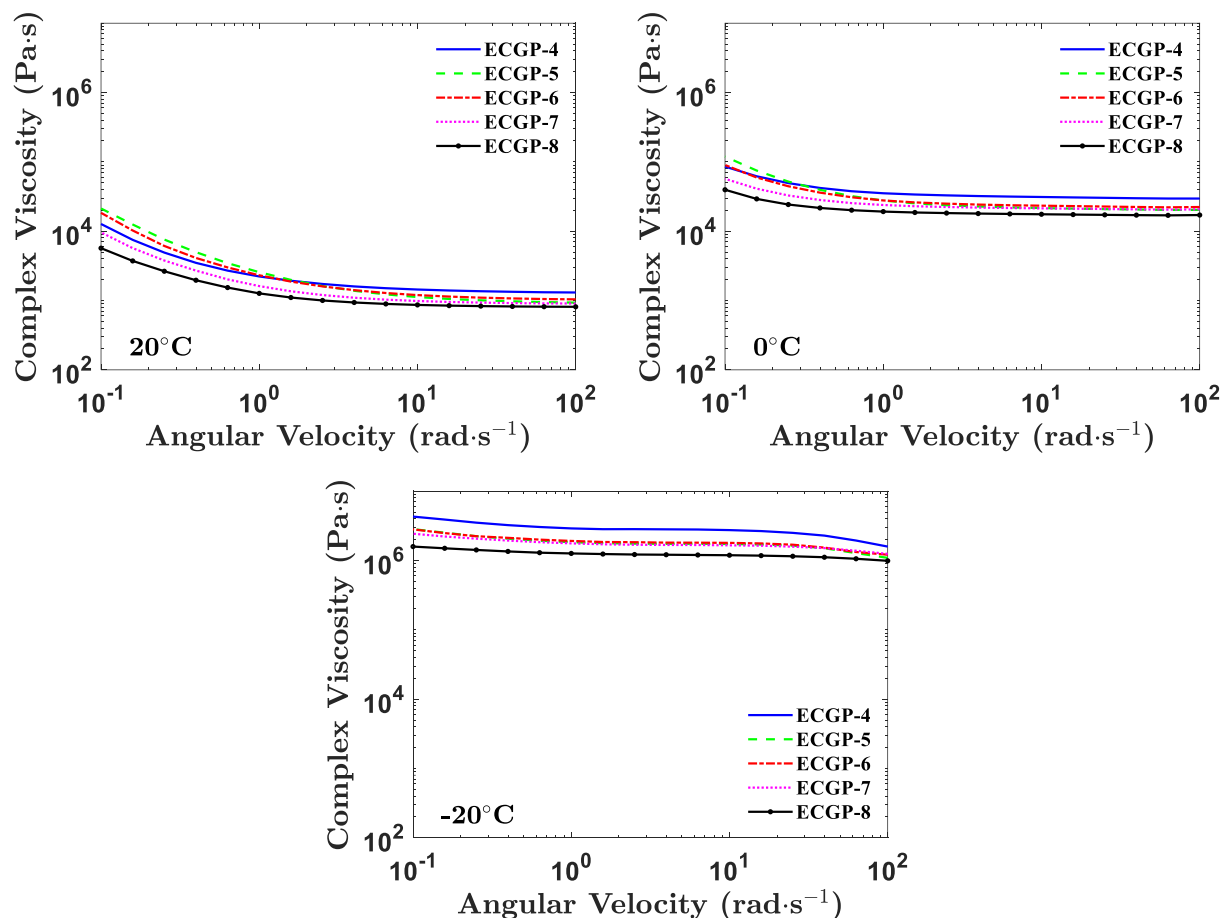


Figure G2.5. Viscosity data for propellants at 20 °C, 0 °C, and -20 °C (clockwise from top left)

G2.2.2 Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy (EIS) study was completed using an Autolab PGSTAT302N potentiostat to determine the resistivity of the gels. Data collected is used to explain the trends seen in the ignition delay study, as a gel with higher resistivity is expected to have a longer ignition delay. A small sample of each propellant was placed in an open-ended ceramic tube and contained between two cylindrical graphite electrodes inserted at both ends. The electrodes were then connected to the potentiostat which applies an oscillating voltage potential to conduct electrochemical impedance measurements over a range of frequencies. The resulting measurements include the real and imaginary impedances, which are found by the potentiostat according to the applied voltage potential and current density reading, expressed as $\psi_s(t)$ and $j_s(t)$ respectively in the following equations (Careem, 2020):

$$\psi_s(t) = \psi_{DC} + \psi_0 e^{i2\pi ft} \quad (\text{G2.1})$$

$$j_s(t) = j_{DC} + j_0 e^{i[2\pi ft - \phi(f)]} \quad (\text{G2.2})$$

Here, ψ_{DC} and j_{DC} are the time-invariant DC voltage potential and current density, respectively, ψ_0 and j_0 are the time-invariant amplitudes of the oscillatory voltage and current density, and $\phi(f)$ is the phase angle between the applied voltage and current density reading as a function of frequency. The total

electrochemical impedance, Z , can then be written in terms of its real and imaginary components, as well as the Euler formula in the following manner (Mei, 2018):

$$Z = Z' + iZ'' = \frac{\psi_0}{j_0} * e^{i\phi(f)} \quad (\text{G2.3})$$

The imaginary component, $-Z''$, can be plotted as a function of the real component, Z' , in a Nyquist plot which depicts a semicircle over high frequencies followed by a linear relationship in the intermediate range of frequencies. An example for ECGP-6 is given in Fig. G2.6 below. The interior cusp of the graph occurs for minimum imaginary impedance, which is a point at which the real impedance can be interpreted as the internal resistance of the gel (Lei, 2013).

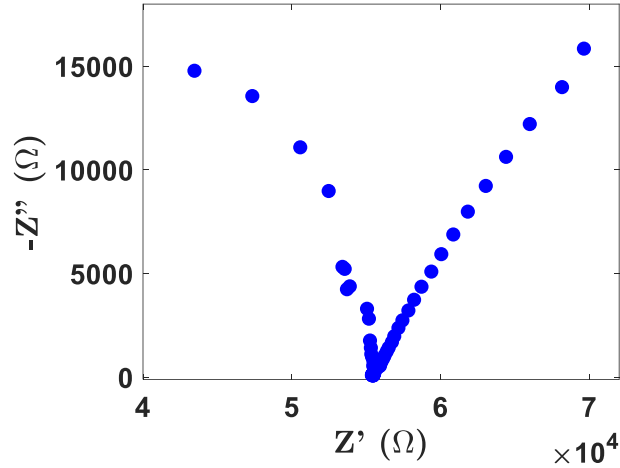


Figure G2.6. Nyquist plot of ECGP-6.

The internal resistance is a property that is dependent on both the length and cross-sectional area of gel subject to the oscillating voltage; to use this data to describe the electrochemical properties of the gel, it is converted to resistivity using Eqn. G2.4 below, where R is the measured real impedance, A is the cross-sectional area of the electrodes, and L is the length of the sample between electrodes. This measurement is a property that describes the ease of transportation of ions through the gels and is in units of ohmmeters.

$$\rho = \frac{RA}{L} \quad (\text{G2.4})$$

The results of the EIS study include the average resistivity and standard deviation over three experiments for each ECGP. The resistivity of a material is the reciprocal of its conductivity, meaning that materials with higher resistivity more strongly resist the transportation of ions within. These findings are reported in Table G2.2 below and show that the average resistivity of the gels increased as AP content increased.

Table G2.2. Average resistivity for ECGP compositions

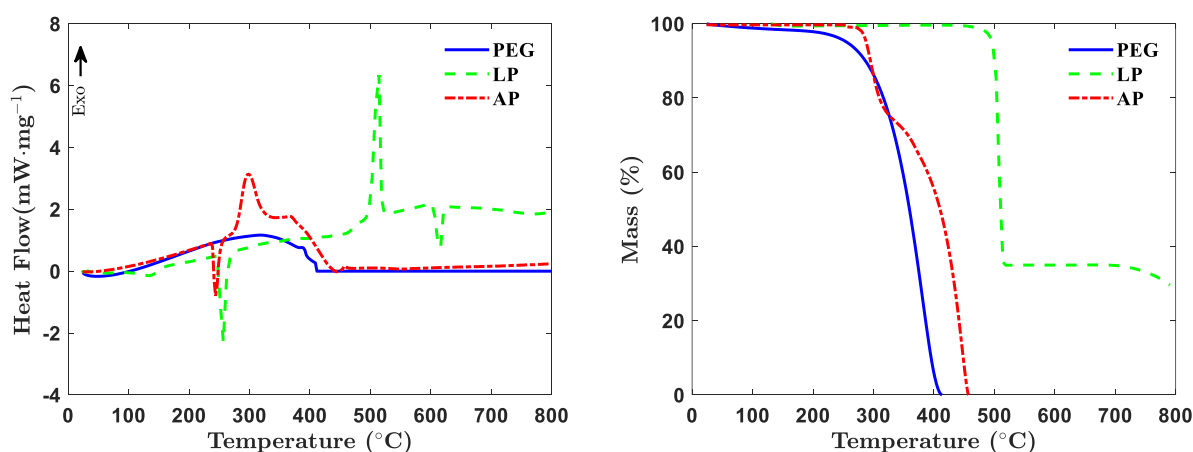
Propellant	Average Resistivity ($\Omega \cdot m$)	Standard Deviation
ECGP-4	225.57	10.0
ECGP-5	273.19	10.9
ECGP-6	325.59	10.7
ECGP-7	389.00	5.1
ECGP-8	485.43	7.4

G2.2.3 Thermal Characterization

Simultaneous Thermogravimetric Analysis/Differential Scanning Calorimetry (TGA/DSC) was conducted using a Netzsch STA 449 F5 Jupiter TGA/DSC for the monopropellants and their individual constituents. The compositions were weighed and placed into an aluminum oxide crucible for experimentation. Each monopropellant sample was subjected to temperature increasing from 20°C to 800°C at a heating rate of 10°C per minute with a continuous nitrogen purge.

The thermal decomposition data for the individual constituents of the ECGPs found in Fig. G2.7 are used to provide context to the results for the ECGPs, which are subsequently depicted in Fig. G2.8. In the constituents, AP is shown to have a notably lower thermal decomposition temperature than LP, which occurs at about 300°C as opposed to 500°C.

In the monopropellants, the initial mass loss between 90 and 160°C is attributed to acetonitrile that is retained in the gel. While the solvent has a boiling point of 82°C, it has been noted in studies that a bond forms between acetonitrile and ions, such as Li^+ , prolonging its evaporation (Commariieu, 2019; O'Donnell, 1965). The onset of the primary exothermic peak for ECGP-4 occurs around 310°C and is seen to shift toward lower temperatures as AP is added. This is caused by the lower thermal decomposition temperature of AP displayed in Fig. G2.7, at which point it is able to react exothermically with the polymer fuel, leading to decreasing decomposition temperatures in the monopropellants as AP content increases. Lastly, the endothermic reaction that occurs above 600°C is attributed to the melting of the lithium chloride which is produced in the primary exothermic reaction of LP (Markowitz, 1964).

**Figure G2.7. DSC and TGA results for the constituents of ECGPs.**

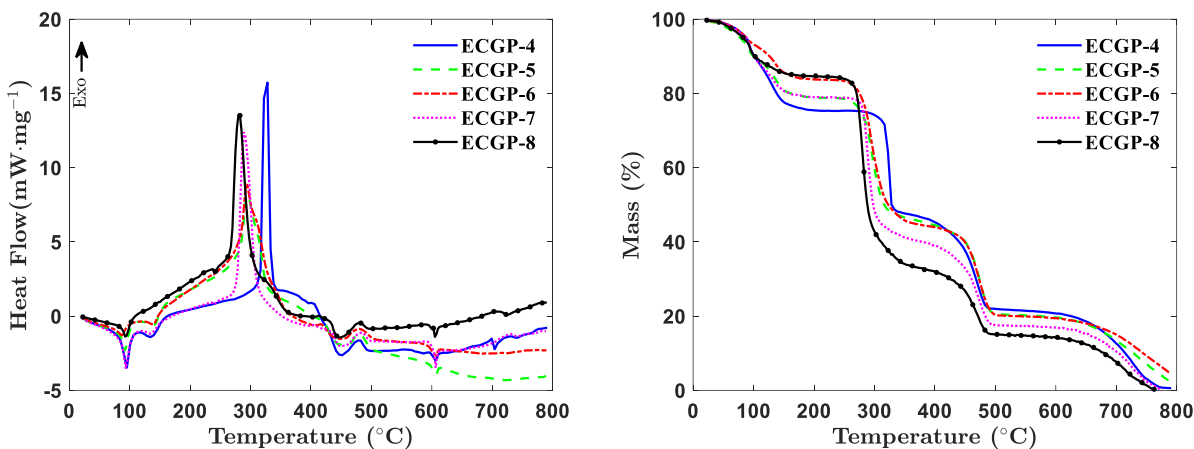


Figure G2.8. DSC and TGA results for ECGPs.

G2.3 Results and Discussion

G2.3.1 Ignition Study

In the ignition study of the ECGPs, the gels are extruded along parallel electrodes which apply the voltage from the power supply to the propellant. After being in contact with the electrodes for some time, the propellants begin to decompose into gases and ignite. Figure G2.9 is a sequence of images attained by high-speed cinematography depicting this combustion process in ECGP-6 with an applied voltage of 140V. At time $t = 0$ seconds, the gel makes its initial contact with the electrodes. The gel advances through the channel, and at time $t = 13.2$ seconds, begins to decompose at the gel front, producing gases seen in the form of bubbles. Shortly thereafter, the gel ignites at time $t = 13.9$ seconds within the decomposition zone near the cathode. By time $t = 14.7$ seconds, a sustained flame is present. Additionally, Fig. G2.10 depicts the current draw of the same experiment, showing that current increases sharply once decomposition is achieved and peaks at the point of ignition.

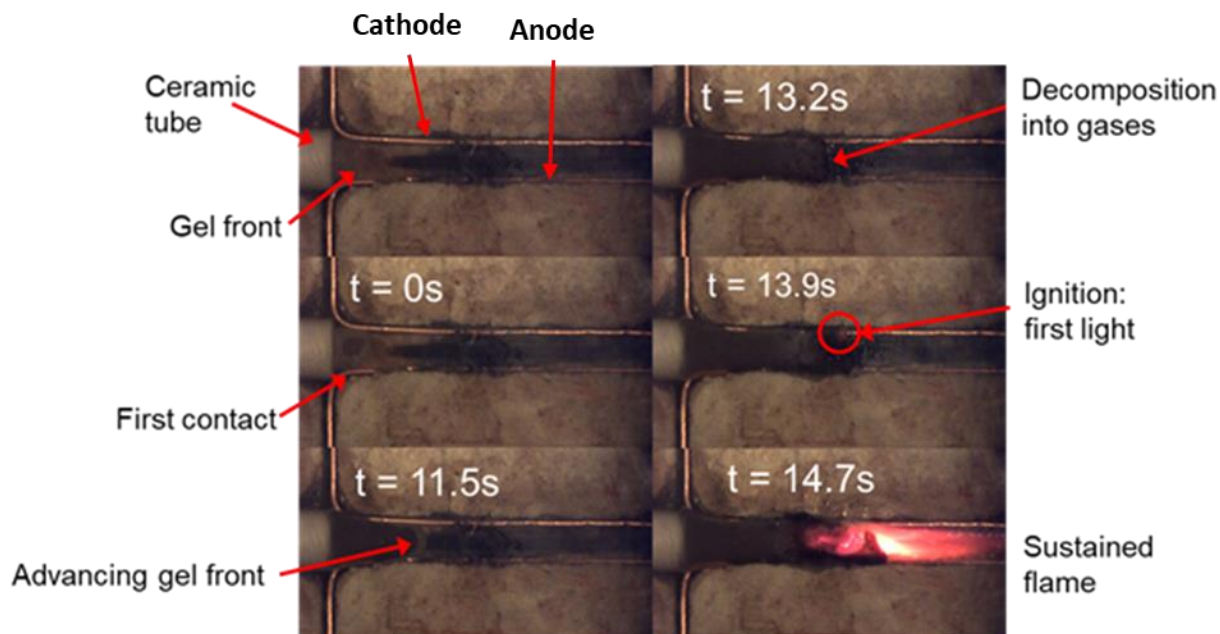


Figure G2.9. Electrolytic combustion of ECGP-6 at 140V

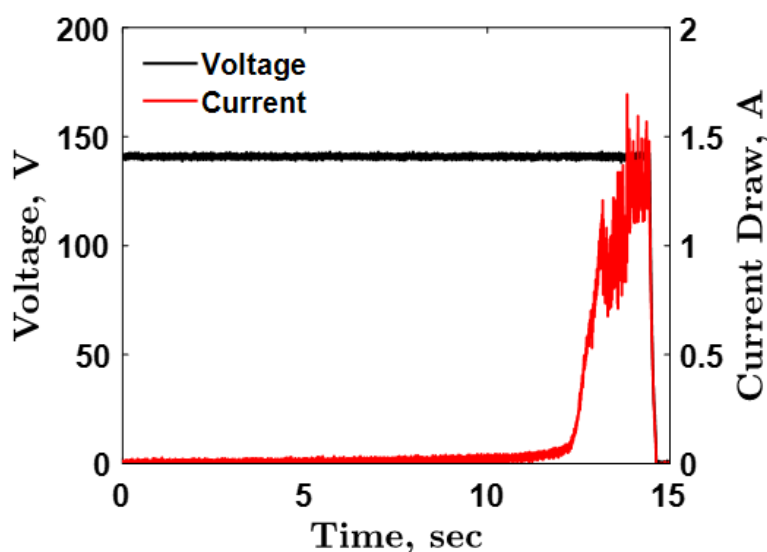


Figure G2.10 Current draw during the electrolytic combustion of ECGP-6 at 140V

The results of this ignition study are depicted in Fig. G2.11, which shows the dependence of the ignition delay on the magnitude of the applied voltage for the different compositions as well as the dependence of the ignition delay on electrode spacing found for ECGP-4. The data points represented are the average times to ignition over at least three experiments and the error bars represent the standard deviation.

Across all ECGPs, the ignition delay decreased with increasing applied voltage. ECGP-5 and ECGP-6 experienced less change in ignition delay as voltage changed, while ECGP-4 is shown to have had the highest sensitivity to changes in voltage. This can be expected as ECGP-4 had the highest ionic conductivity. With the presence of small amounts of AP, the ignition delay is seen to decrease. However, as AP content continues to increase, the ignition delay increased across voltages. At 120V, ECGP-4, ECGP-7,

and ECGP-8 failed to ignite and only showed subtle signs of decomposition. Additionally, the ignition delay of ECGP-4 was found to decrease with decreasing electrode spacing, which is a result of increased current density, accelerating the electrolytic reaction (Khane, 2015).

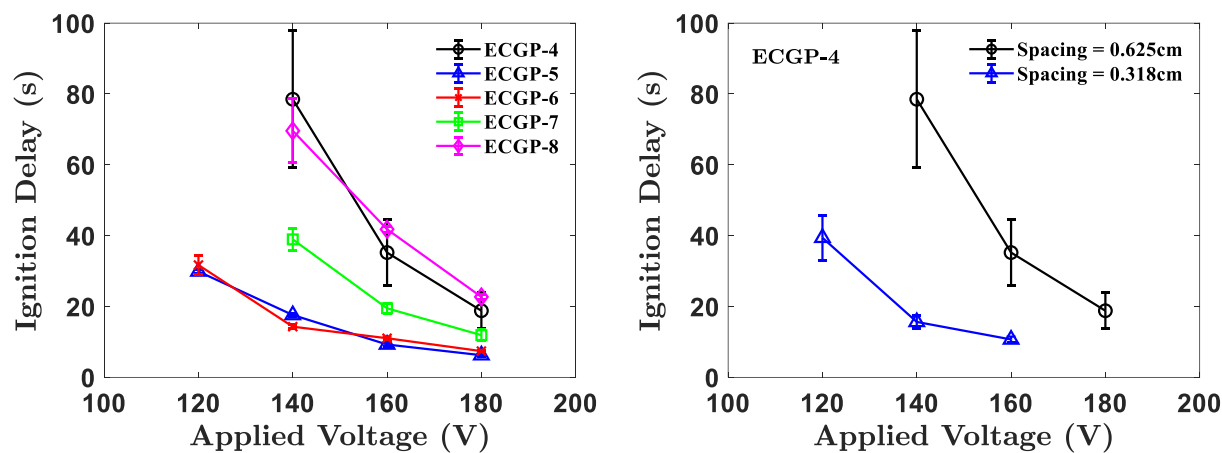


Figure G2.11 Ignition delay data for ECGPs.

The ignition of the gels is believed to be facilitated by competing thermal and electrochemical mechanisms. The applied voltage charges the GPE, causing the lithium cation to flow toward the cathode while the perchlorate anion flows to the anode. At the cathode, the cations are reduced, gaining an electron in an exothermic reaction. The oxidation of the perchlorate anion occurs at the anode, in which it loses an electron. These electrochemical mechanisms are described further in the study completed by Gobin et al. (Gobin, 2022). Ohmic heating exists in the presence of current and appears to contribute to the overall ignition process to varying degrees. On its own, this is a thermal process whereby the ignition of the gels would be facilitated in a similar manner to the previously discussed TGA and DSC results.

It is known that the Li^+ ions migrate to the cathode by hopping through the O-sites of PEG. The FTIR peaks associated with ClO_4 groups in $\text{LiClO}_4/\text{PEG}$ are red shifted by 30 cm^{-1} and 20 cm^{-1} respectively from their positions in bare LiClO_4 , as shown in Fig. G.12. This indicates the weakening of the chlorine-oxygen bonds, which we attribute to the attractive interactions of Li^+ with the oxygen atoms in PEG. Such complexation between the Li^+ and the O-groups of PEG will both promote gelation, and the migration of Li^+ to the cathode. To analyze the products formed during the electrochemical reactions, the electrolysis process was stopped before the ignition event and the cathode was characterized under an optical microscope and ATR-FTIR, which is shown in Fig. G.12. Here, a black Li deposition on the cathode is depicted, which becomes white upon prolonged exposure to the ambient atmosphere. The FTIR spectrum of the cathode with the white depositions shows a characteristic sharp peak of Li-OH , implying that Li is electrochemically reduced at the cathode, which when exposed to air is oxidized.

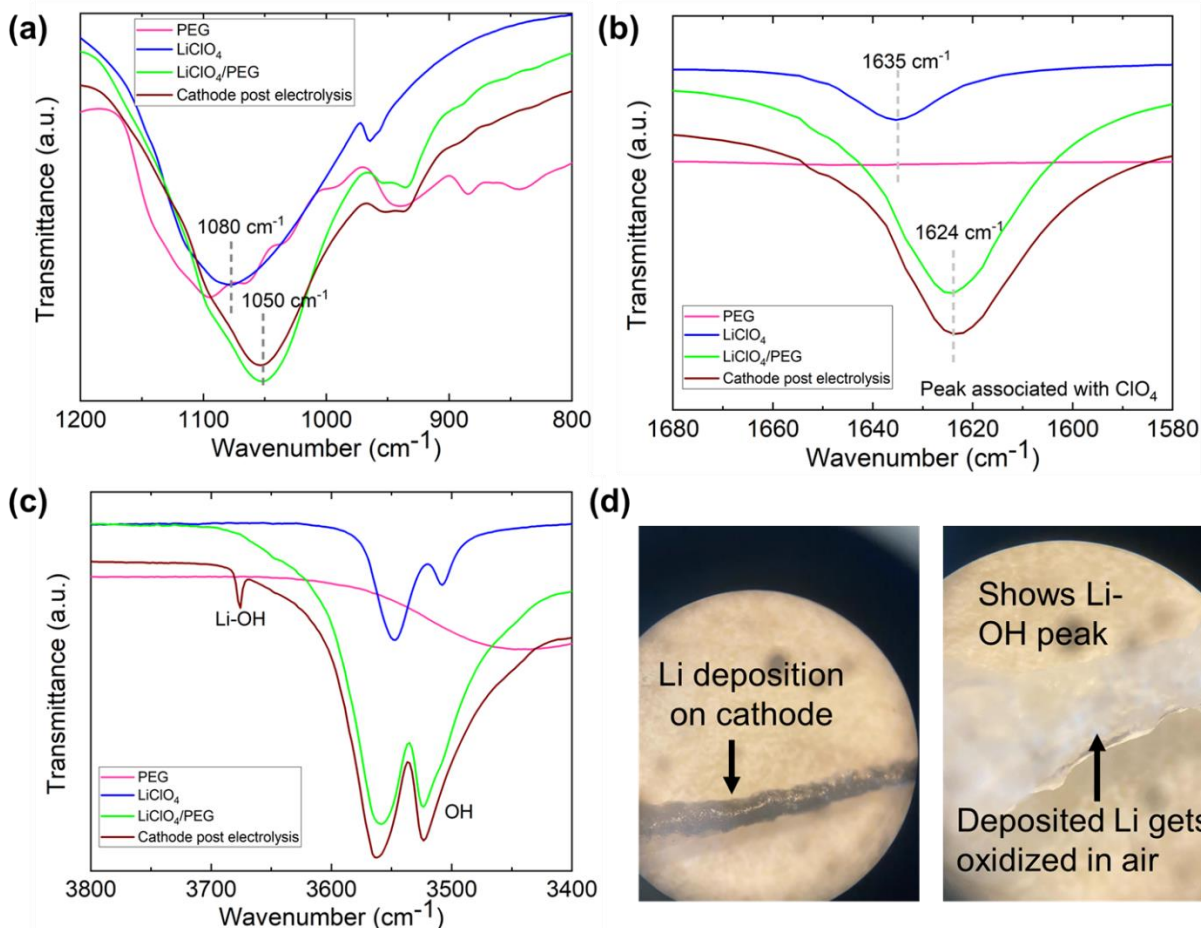


Figure G.12 FTIR peaks associated with ClO_4 group in ECGP-4 is redshifted by (a) 30 cm^{-1} and (b) 20 cm^{-1} from neat LiClO_4 indicating complexation of LiClO_4 with PEG; (c) sharp Li-OH peak observed in the FTIR spectrum of the cathode post-electrolysis, confirming the deposition of Li on cathode on its reduction; and (d) optical microscope images of the Li deposition on cathode after electrochemical reaction.

Figure G2.13 depicts IR thermometry on the electrodes during the electrolysis process show that the cathode heats up first leading to heat diffusion to the surroundings. Over time, the hot-spot at the cathode reaches about 350°C , which is above the onset point of the exothermic reaction in ECGP-4 shown in Fig. G2.8. Hence, it appears that the hotspot at the cathode initiates exothermic reactions resulting in the ignition of ECGPs at the cathode.

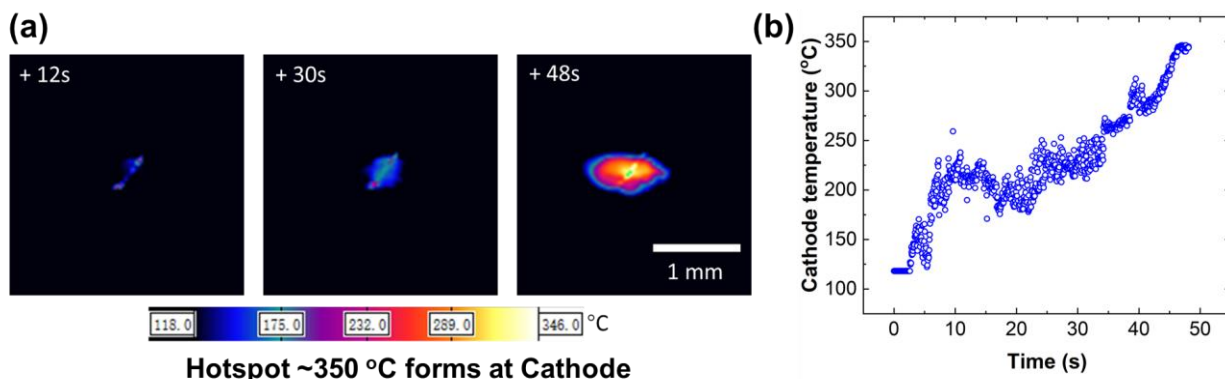


Figure G2.13. (a) Time resolved IR thermograph shows the hotspot formation at the cathode and (b) the maximum temperature on the cathode increases with time and reaches the ignition temperature of PEG.

G2.3.2 Pressure Study

The combustion of ECGP-4, ECGP-6, and ECGP-8 was studied under pressure in an optically accessible strand burner with a nitrogen purge to determine the pressure deflagration limit and the corresponding burn rate for each. The burn rate was determined using a burn trajectory by measuring the distance that the center of the combustion front advanced toward the base of the sample carrier at multiple time intervals with knowledge of a reference distance $X_{ref} = 15.7$ mm. Figure G2.14 shows the regression of ECGP-8 at its determined PDL of 0.345 MPa. Time $t = 0$ seconds serves as a reference at which the igniter propellant had been consumed and the gel was first seen burning on its own. Between times $t = 15.3$ and $t = 61.1$ seconds, the combustion front of the gel regresses about 16.1 mm. Time $t = 61.1$ seconds shows the end of the propellant burn, at which point the gel is completely consumed.

The results of this study are recorded in Table G2.3. Because burn rate data was collected at the respective PDL of each monopropellant examined, these results are not directly comparable. Due to AP's enhancement of burn rate when paired with LP, it can be expected that an increase in AP content would lead to higher burn rates at any given pressure (Gobin, 2021).

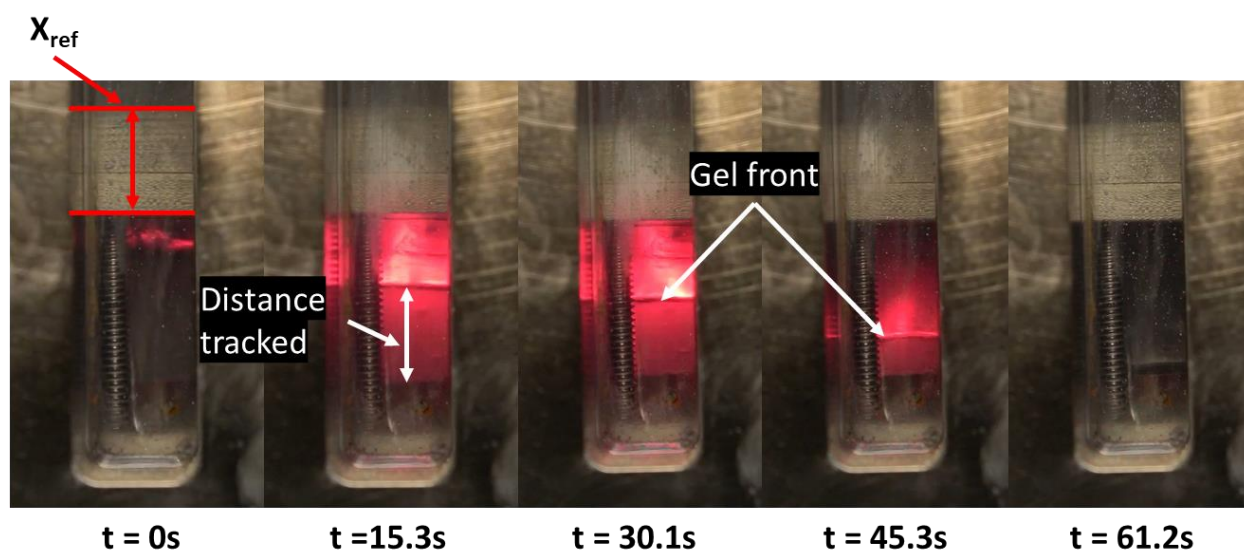


Figure G2.14. Regression of ECGP-8 at 0.345 MPa.

Table G2.3. Pressure deflagration limit and corresponding regression rate for select candidates.

Candidate Name	Pressure Deflagration Limit (MPa)	Regression Rate at PDL (mm/s)	Standard Deviation
ECGP-4	2.41	0.637	0.13
ECGP-6	1.03	0.896	0.11
ECGP-8	0.345	0.357	0.0077

G2.4 Conclusions

An investigation of the effects of the addition of ammonium perchlorate at a fixed polymer-to-oxidizer ratio on the material and combustion properties of an electrically controlled monopropellant composed of a gel polymer electrolyte was completed. Due to their ionic conductivity, the gel monopropellants are able to use electrolytic mechanisms to decompose and ignite with an applied voltage potential.

Material properties that were characterized include the monopropellants' rheology as a function of temperature, their conductivity in an EIS study, and their thermal decomposition using simultaneous TGA/DSC. It was found that increasing AP content decreased the viscosity of the gels. The increase in AP content was seen to decrease their ionic conductivity, which had a direct impact on their electrolytic ignition delay. The primary thermal decomposition temperature decreased with an increased presence of AP, reflecting the lower decomposition of AP when compared to LP and its exothermic reaction with the polymer fuel. These material properties were further used to understand combustion characteristics of the monopropellants.

The electrolytic ignition delay of the monopropellants was shown to be sensitive to oxidizer content, voltage magnitude, and electrode spacing. As the conductivity of the gels decreased, the electrolysis process was slowed, and the ignition delay was prolonged. This showed that the ignition of the gels with an applied voltage was characterized by competing electrochemical and thermal processes. Additionally, both the increase in applied voltage magnitude and decrease in electrode spacing were shown to enhance the electrolysis of the gels, facilitating their ignition. At elevated pressures, the increase in AP content was shown to decrease the pressure deflagration limit of the gels.

Solid Propellant Study 1 "S1"

The objective of the research outlined in this paper is to study the relationship between the applied power and the burning rate of various ECSPs utilizing a SPE. The host polymer matrix of interest is PEO, and the oxidizer salts are LP and AP. The composition of the various ECSPs are changed to develop a relationship between the composition, their response, and burning rate. A focus was placed on gaining an understanding of the fundamental mechanisms that are present in the electrochemical decomposition of the ECSPs that enable an accelerated decomposition.

S1.1 Methods

S1.1.1 Sample Preparation

The polymer, PEO was purchased from Sigma-Aldrich and had a viscosity average molar weight of 200,000 g/mol. The solid oxidizers under consideration in this study were 200 μ m LP and AP, both of which were purchased from Firefox Enterprises and had a stated purity of over 99.0%. AP and LP were selected as they possess oxidative properties and are soluble in PEO (Gray, 1991). The solvent used was acetonitrile, which was purchased from Fisher Scientific and had a purity of 99.9%.

The ECSPs were created by placing the desired amount of acetonitrile on a stir plate, after which the desired amount of PEO was added and stirred until the polymer was completely dissolved. Once the polymer was dissolved, the desired amount of AP and LP were added and stirred until sufficiently dissolved. The solution was then cast into a 12.7x12.7x25 mm rectangular prism mold and allowed to cure for one week. The composition of the ECSPs used in the experiments are outlined in Table S1. Qualitatively, ECSPs using only LP as the oxidizer suffered from poor mechanical properties when the PEO content was increased over 22.5%. Similarly, when AP was included as an oxidizer, ECSPs with more than 12.5% by weight PEO also had poor mechanical properties. PEO is known to be a hygroscopic polymer (Baird, 2010), and we attribute the poor mechanical properties to this fact, which was further exacerbated by the inclusion of AP.

Table S1.1 ECSP Sample Composition

Sample Name	Percent PEO	Percent LP	Percent AP
SP1	22.5	77.5	0
SP2	20	80	0
SP3	12.5	87.5	0
SP4	12.5	43.75	43.75
SP5	10	90	0
SP6	10	45	45

S1.1.2 ECSP Resistance

The resistance of the melt phase of the ECSPs can be determined by the voltage and current draw during each experiment. However, in the case of the solid phase of the ECSPs, additional experiments in the form of impedance spectroscopy are required to ensure accurate resistance values. The impedance spectroscopy experiments were conducted using an Autolab PGSTAT302N. Briefly summarized, impedance spectroscopy utilizes a low magnitude alternating voltage which is applied across a sample and the resulting current draw is measured (Careem, 2020). The frequency of the alternating current response is the same as that of the applied voltage but offset by some angle (θ) (Careem, 2020). The magnitudes of the voltage (v_0) and current (i_0) at a given frequency gives the magnitude of the impedance (Z_0) as defined by (Careem, 2020).

$$Z_0 = \frac{v_0}{i_0} \quad (S1.1)$$

The impedance can then be further broken down into its real (Z') and imaginary (Z'') parts defined as (Careem, 2020).

$$Z' = Z_0 \cos \theta \quad (S1.2)$$

$$Z'' = Z_0 \sin \theta \quad (S1.3)$$

Calculating and plotting the real and imaginary impedance for a range of frequencies gives what is referred to as a complex impedance plane plot, an example of which is shown in Fig. S1.1 for the SP2 composition. The nonzero intercept of the plot with the real Z' impedance axis gives the resistance for that given sample (Careem, 2020).

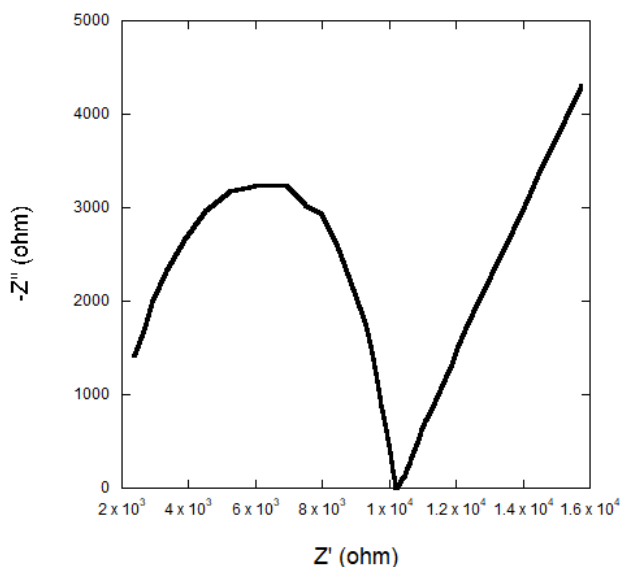


Fig. S1.1 Complex Impedance Plane Plot for SP2

S.1.1.3 Imaging

Scanning electron microscopy was utilized to gain insight into how the changing of the composition effects the morphology of the samples. The scanning electron microscope (SEM) used was the JEOL JSM-IT500. Each of the ECSPs were coated in 10nm of platinum and palladium and an accelerating voltage of 5kV was used. An energy dispersive x-ray spectrometer (EDS) was equipped in the SEM and was utilized to gain an understanding of the composition of various features found during the SEM imaging.

S1.1.4 Combustion and Regression Rate Experiments

In order to gain an understanding of the combustion characteristics of the ECSPs listed in Table S1.1, each ECSP was loaded into an experimental apparatus shown in Fig. S1.2. All experiments were conducted at atmospheric pressure and in an open-air environment. The experimental apparatus comprised an electrically isolating ceramic channel base that the ECSP sample was loaded into in order to contain the combustion reaction. Two 6mm wide copper plate electrodes were placed at the end of the channel 12.7 mm apart to allow for a voltage potential to be applied across the ECSP sample. The ceramic base had locating features to ensure that the electrodes were placed at a consistent location and did not move during the experiment. A ceramic rod was attached to a pusher plate which had tension springs to ensure the ECSPs maintain contact with the electrodes and continues to feed new material into the electrodes for consumption. The ECSP samples have a 6mm by 12.7 mm contact area with each electrode throughout the experiment. The pusher plate was connected to a linear variable displacement transducer (LVDT), which was used to track the displacement of the samples during the course of the experiment as they are consumed. To quantify how quickly a given sample was being consumed by the electrochemical decomposition, the linear

regression rate was calculated from the change in the displacement (y) of the LVDT over a span of time (t) as shown in Fig. S1.3

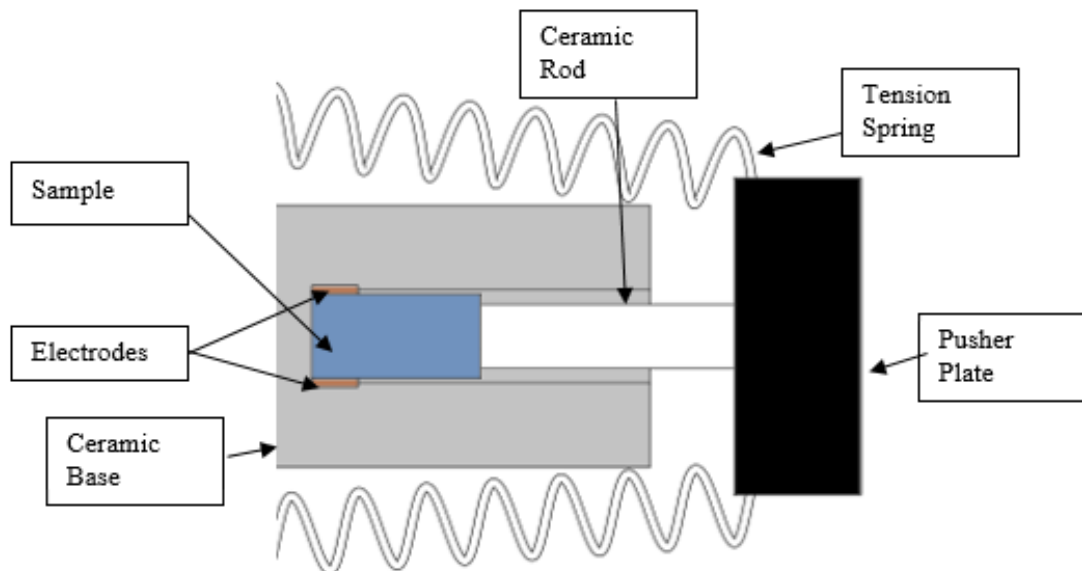


Fig. S1.2 ECSP Experiment Configuration

The primary focus of the combustion experiments was to observe the effects of an applied voltage potential on the regression rate and response time for each ECSP composition. The goal of each ECSP was to develop a composition that would ignite rapidly through electrochemical means but would not ignite through thermal loads. This would allow for the creation of an ECSP that would be easier to quench if the applied electrical load were to be removed.

Each combustion experiment was conducted by loading a solid ECSP sample into the ceramic base and ensuring that the copper electrode had sufficient contact with the sides of the ECSP. A predetermined voltage was applied to the electrodes, which initiated the experiment. The voltage was applied using a XP Power HPT5K0-L DC power supply, whose voltage output during the experiment was measured and recorded using a voltage step down circuit and a National Instruments SCB-68A data acquisition unit (DAQ). A Fluke i50s current probe was used to measure the current draw resulting from the applied voltage, which was recorded using the DAQ. The DAQ also records the measured displacement of the LVDT throughout the course of the experiment. The regression rate was found using the method shown in Fig. S1.3 for the range at which steady combustion was achieved. For the range selected in the regression rate calculation, the average of the current and voltage was extracted from the raw data. The experiments were also recorded using a Phantom VEO 7.10L high speed camera in order to gain insight into the ignition process as well as the interactions that occur in the melt layer of the propellant and at the electrodes.

Figure S1.3 shows an example of the data captured during the course of an experiment. In the experiment shown in Fig. S1.3, the voltage was turned on at $t=0$ seconds and due to the ECSP samples being conductive in their solid state, ions began to flow immediately as shown by the nonzero current draw value at $t=0$. At $t=1$, it can be seen that the displacement began to change corresponding to the ECSP sample being consumed. This initial displacement is usually caused by the initial melting and decomposition that takes place once the power is turned on, prior to ignition. At around 1.6 seconds, ignition was achieved as shown by the rapid decrease in the current draw due to the burning phase having large amounts of gaseous

products that increases the resistance. Beyond $t=2$ seconds, steady burning was achieved as shown by a relatively smooth displacement curve and a relatively constant current draw.

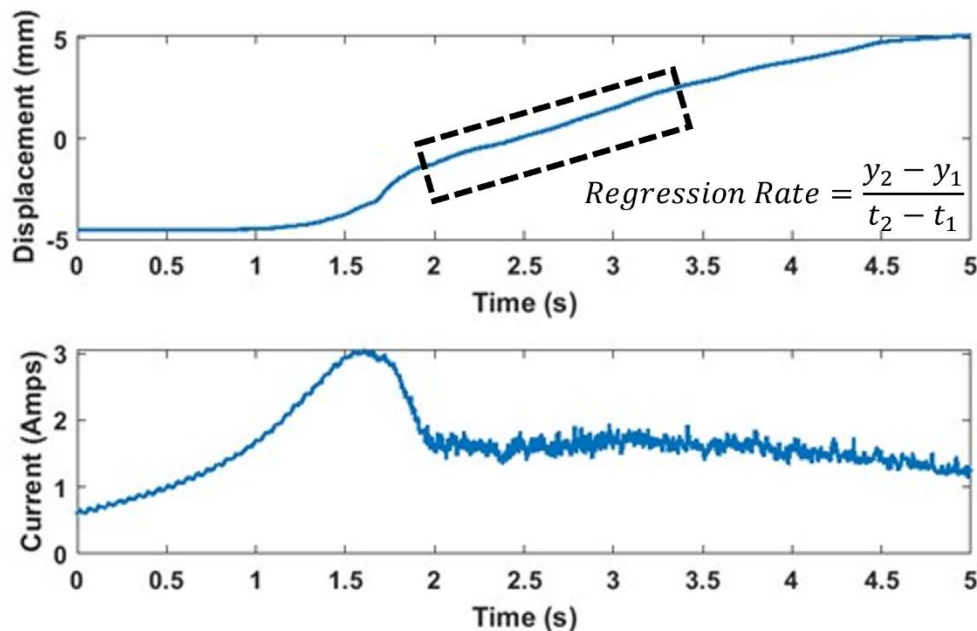


Fig. S1.3. ECSP Displacement and Current

Additional experiments were conducted using ECSP samples that were cast into 25x12.7x25 mm and 38x12.7x25 mm rectangular prism molds. These experiments utilized a similar experimental configuration as that shown in Fig. S1.2, with the exception that the plate electrodes were placed 25 and 38mm apart respectively. This was done to analyze the sensitivity of the ECSPs to the spacing of the electrodes that are applying the voltage potential.

S1.2 Results

S1.2.1 Regression Rate

To determine the ability of each ECSP to ignite by thermal means, a butane torch lighter was used to attempt to achieve thermal ignition. None of the ECSP samples created achieved ignition and self-sustaining combustion by thermal stimuli. However, the application of power to the ECSPs resulted in a rapid decomposition and ignition for all the samples used in the experiments. This indicates that the ECSPs require the ionic decomposition brought on by a voltage potential to sustain a flame. The resulting regression rate for SP5 and SP6 is shown in Fig. S1.4 s as a function of the applied voltage. These plots clearly show a steady increase in the regression rate as the voltage potential is increased in each sample. The increase in regression rate as the voltage increases is due to the increase in the rate of ion flow at higher voltages resulting from a higher ionic velocity (Bowers, 2021). The ECSP samples that use only LP as its oxidizer (SP1/SP2/SP3/SP5) show a linear relationship between the regression rate and the applied voltage magnitude. The electrode spacing was held constant during each experiment. The ECSP samples that use AP along with LP as its oxidizer (SP4/SP6) show a nonlinear relationship between the regression rate and applied voltage. The regression rate of SP4 and SP6 are similar in magnitude to the other compositions for voltages below 180V, however at 200V the regression rate sharply increases relative to all other

compositions. This suggests that at lower voltages, the addition of AP does not contribute significantly to the regression rate, but at higher voltages the contribution becomes very significant. Since AP is more thermally energetic than LP (Gilliand, 1961), its decomposition contributes greater to the heat feedback in the system accelerating the reaction. This behavior becomes more pronounced at higher voltages due to the higher voltages resulting in a higher ionic velocity (Bowers, 2021) and accelerating the reactions which produces higher heat feedback and causes the AP decomposition to accelerate.

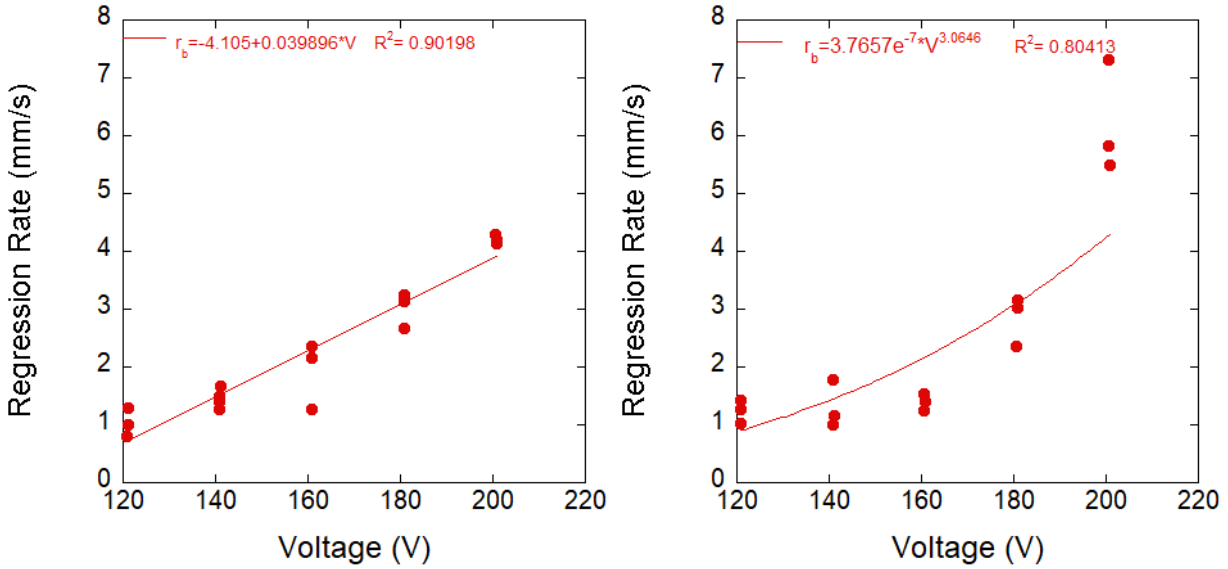


Fig. S1.4. ECSP Regression Rate vs. Voltage for SP5 (left) and SP6 (right)

Multiplying the measured current draw by the applied voltage for a given sample provides the applied power. The relationship between regression rate and applied power was found to follow a power law relation, similar to St. Robert's Burning Rate Law that is used to relate regression rate and pressure as shown in Eq. (S1.4) (Kershner, 1970). Prior work studying ammonium nitrate and epoxy solid propellants used a similar approach to relate electrical power to regression rate (Zamir, 2021). In Eq. (S1.4), r_b is the regression rate, P is the pressure, and a and n are constants. Replacing the pressure term with an electrical power term (P_e) and using new constants c and m yields the relationship shown in Eq. (S1.5). An example of the power law relationship between the applied electrical power and regression rate is shown in for figure S1.5 SP4. Each point in figure S1.5 corresponds to an individual experimental result. The constants in Eq. (5) for each ECSP composition along with the R^2 coefficient of determination are shown in Table S1.2. The results demonstrate the compositional effects on the burning characteristics of ECSPs.

$$r_b = aP^n \quad (S1.4)$$

$$r_b = cP_e^m \quad (S1.5)$$

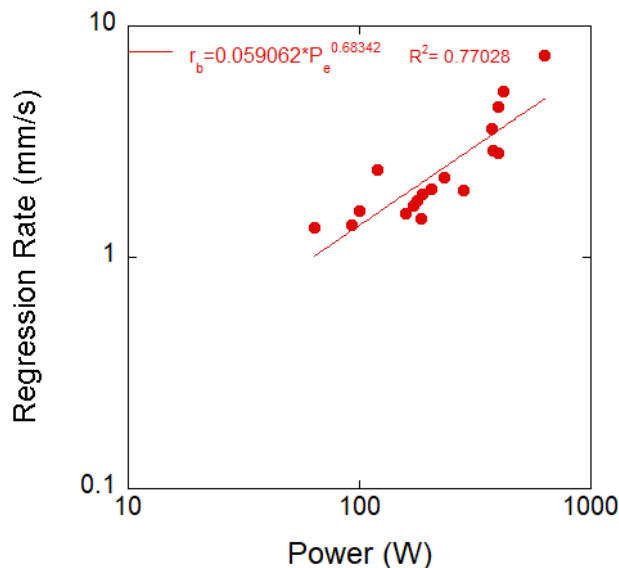


Fig. S1.5. ECSP Regression Rate vs Power for SP4

Table S1.2 Electrical Power vs Regression Rate Power Law Constants for ECSP Compositions

Sample Name	c	m	R ²
SP1	0.00313	1.15	0.91
SP2	0.00755	0.98	0.74
SP3	0.0303	0.75	0.48
SP4	0.0591	0.68	0.77
SP5	0.00361	1.11	0.70
SP6	0.0107	0.95	0.75

Since LP has been used frequently in polymer electrolytes, a great deal of literature exists on potential reaction pathways. When LP is dissolved in PEO, the LP dissociates into its anion and cation as shown in Eq. (S1.6) (Watanabe, 1986). The dissociation is caused by the ether oxygen atoms in the PEO matrix, which complex with the lithium ions (Kotobuki, 2019). These complexation sites enable the movement of the lithium ion when a voltage is applied. With power applied, the lithium ions move toward the cathode where it is reduced as shown in Eq. (S1.7). The perchlorate anions do not move as freely as the lithium cations, but its movement cannot be neglected (Watanabe, 1986). The perchlorate anions produce diatomic oxygen at the anode by Eq. (S1.8) (Hashimi, 1990) when the polymer electrolyte is in its solid phase. Once the polymer electrolyte enters its molten phase the decomposition reaction of the perchlorate ion begins to follow Eq. (S1.9) (Anders, 1968).





This decomposition process differs from the thermal decomposition of LP which yields lithium chloride (LiCl) and 2 diatomic oxygen molecules (Marvin, 1945).

The presence of high concentrations of oxygen leads to a rapid decomposition of many polymer chains, particularly those with back bones comprised of bonds other than the typical carbon-carbon bonds as is the case in PEO (Madorsky, 1959). PEO based electrolytes with lithium salts are known to be unstable under high voltage loads and oxidize at voltages around 3.7V in some instances (Prosini, 1998). This PEO instability is known to occur at the cathode (Simonetti, 2017), and is made worse by the presence of an oxygenated environment (Harding, 2015). In our experiments the applied voltage is substantially higher than the minimum decomposition voltage, which in addition to the high concentration of oxidizers, results in the rapid oxidation of the PEO. This decomposition process was confirmed by the use of high-speed cinematography, which showed the ECSPs beginning to change phase to a liquid at the negatively charged cathode as shown in Fig. 6. The liquid formation is from the chain scission of the PEO backbone which undergoes rapid oxidization (Simonetti, 2017; Harding, 2015). This differs from the electrochemical decomposition process seen in HAN, which favors the anode due to the initiating step being a proton transfer (Wu, 2009). The time $t=0$ seconds in Fig. S1.6 corresponds to a reference time for the sequence shown and not necessarily the time at which power was applied. The transformation to a liquid phase indicates that the backbone of the PEO is beginning to oxidize and break down (Harding, 2015). The oxidation process of PEO initializes with the weaker carbon-oxygen bonds of the backbone breaking, followed by the stronger carbon-carbon bonds breaking (Mirsakiyeva, 2019). As the ECSP decomposes and the current flows, the melt layer grows from the cathode to the anode. The growth of the melt layer is caused by the chain scission of the PEO polymer due to the high applied voltage and interaction with the lithium metal deposits (Andersson, 2021) from Eq. (S1.6). The melt layer growth which connects the two electrodes is the rate limiting step, as once the connection is completed ignition follows shortly. In all experiments conducted in this study, full ignition of an ECSP sample required that the liquid melt layer reached the anode as shown in the $t=0.9$ seconds image in Fig. S1.6. This is likely due to two major factors, the first one being that the ions can flow significantly easier through the liquid layer than the solid layer. This can be seen in Fig. S1.3, where the current draw increases as the melt layer grows due to the decrease in resistance. A higher rate of ions moving through the solution would likely lead to an increase in the decomposition of the PEO polymer backbone. The second factor leading to the ignition occurring once the melt layer connects the electrodes is the increased rate in the perchlorate ion decomposition at the anode. There are no substantial gaseous products observed at the anode until the melt layer connects the anode and cathode. Once the connection is completed, bubbles begin to form around the anode showing that the perchlorate ions are beginning to break down into gaseous oxygen and chlorine, which assist in the ignition of the polymer. Once ignition occurs, the ECSPs reach a steady state combustion process. Following electrochemically aided ignition, the heat caused by the flame results in a combined electrochemical and thermal decomposition. Once the electrical power was removed, the flame extinguished indicating that thermal initiation from the flame alone is not sufficient to self-sustain the reaction. Using the results obtained from our thermochemical analysis with the NASA CEA thermochemical code (Gordon, 1994), the power supplied to the propellant from the flame was estimated to be about 7kW, which is similar in magnitude to estimates of polymer electrolyte fires with less energetic compositions (Chen, 2020). The applied electrical power input in our study was between 60-800W to enable combustion of the ECSPs, which is one to two orders of magnitude lower than the thermal heat feedback. Thermal energy alone does not result in sustained combustion while the application of lower electrical power results in ignition and sustained combustion does. This further suggests that an electrochemical process aids the ignition process.

Similar behavior has been observed with HAN based monopropellants with electrochemical ignition proceeding with a lower activation energy than thermal initiation (Risha, 2007).

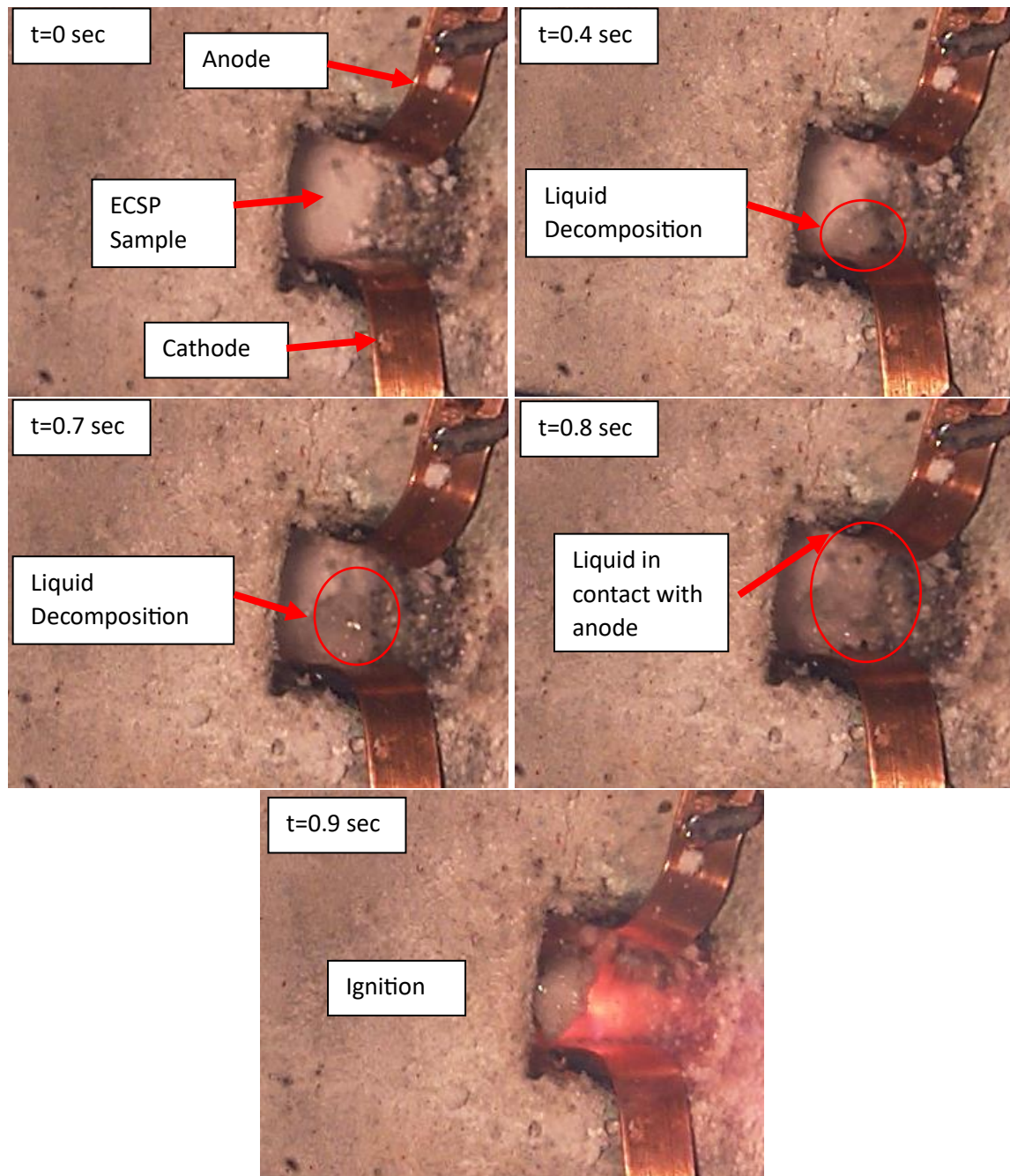


Fig. S1.6. Electrochemical Decomposition Evolution

The copper electrodes are coated in a black layer after the termination of the experiment, which is believed to be copper oxide and lithium oxide/hydroxide. Prior research into the interactions with copper electrodes in molten LP found that layers of black copper oxide form directly on the surface (Denning, 1967). The copper oxide formation on the electrodes forms a passivation layer, which in our prior work was found to decrease the effectiveness of the applied power (Gobin, 2021). Lithium metal has been shown to react with

PEO breaking the carbon oxygen bonds leading to the formation of lithium oxide and lithium hydroxide (Patra, 2018), which is black in color (Mirsakiyeva, 2019; Pervez, 2019). The lithium metal is formed from the reaction described in Eq. (S1.7) and helps to accelerate the PEO decomposition.

Dissolving AP into PEO results in AP breaking down into its anion and cation as defined by Eq. (S1.10) due to the complexing between the PEO and AP. The complexing is caused by the ammonium cation interacting with the oxygen in the PEO back bone, similar to that seen in LP. The perchlorate ions in AP follow a similar decomposition as that found in LP as shown in Eq. (8) and Eq. (9). The ammonium ions do not easily flow in a solid polymer electrolyte, due partially to their larger size. Small ions such as protons and lithium ions are generally preferred in electrolytes due to their higher mobility (Yusuf, 2019). The addition of ammonium ions, instead tend to create a proton (H^+) conducting polymer (Hashimi, 1990). Proton conduction is caused by the hopping of the weakly bonded hydrogen in the ammonium via the coordinating sites as shown in Fig. S1.7 (Hashimi, 1990). The protons are then reduced at the cathode to yield hydrogen gas as shown in Eq. (S1.11).



The electrochemical decomposition of AP differs from the proton transfer initiating step that is associated with thermal decomposition when the heating rate is high, which yields perchloric acid and ammonia (Kubota, 2007). The decomposition process of the propellants with AP and LP follows a similar trend as the samples only with LP, where the decomposition begins at the cathode and ignition occurs shortly after the melt layer reaches the anode.

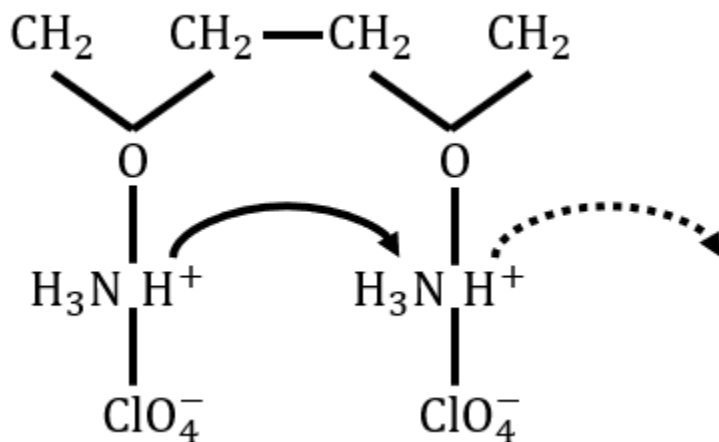


Fig. S1.7. Proton Transport Mechanism in PEO (Hashimi, 1990)

As the magnitude of the applied voltage potential increases, the time required to achieve a steady state flame is drastically decreased in atmospheric pressures as shown in Fig. S1.8. A steady flame is defined as the time when the regression rate is nearly constant, and the combustion is in a nearly steady state. Each data point in Fig. S1.8 is an average of 3 values. At low voltages around 120V, it was common for a sample take 10 seconds to achieve steady burning. In these low voltage conditions, the sample would initially melt as soon as the power was applied. Then after a short delay, the ECSP sample would begin to decompose and smoke, but would take much longer to ignite. This delay is due to the time required for the formation of a melt layer that starts at the cathode and moves towards the anode as discussed previously. Once the

voltage potential was raised to the 180-200V range, it was common to achieve a steady state flame in one second or less, which would be a more practical time delay for use in a solid rocket motor.

The ignition delay, or time between power on and first light, decreases as the magnitude of the applied voltage increases due to the relationship between ionic velocity (v) and the applied electric field (E) defined as (Bowers, 2021).

$$E = \frac{V}{L} \quad (S1.12)$$

$$v = \mu E \quad (S1.13)$$

Where V is the magnitude of the applied voltage, L is the length over the voltage is applied, and μ is the mobility of the charge carriers through the medium. Using the relationships from Eq. (S1.12) and Eq. (S1.13), it can be seen that as the applied voltage increases, the rate at which the ions move also increases. Due to the movement of ions being the cause of the initial decomposition of the PEO backbone, an accelerated ion movement rate would lead to an accelerated decomposition rate and an earlier ignition. The increased ion velocity and voltage relation also helps to explain why the regression rate increases as the voltage applied increases.

To further verify this claim, additional experiments were conducted using SP4 but using electrodes that were placed 25 or 38mm apart and using samples that had a cross section of 12.7x25mm or 12.7x38mm respectively. Three experiments were conducted at each electrode spacing. By increasing the spacing between electrodes, this led to a large increase in the time to achieve a steady burn. The steady state delay went from 0.7 seconds for a 12.7mm spacing to 8 seconds for a 25mm, to 33 seconds for 38mm electrode spacing at 200V. The large increase in the steady state delay was due to the length decreasing the electric field as shown in Eq. (S1.12), and also the increased distance the melt layer has to travel to connect the anode and cathode. This results in a melt layer that forms slower and has to travel further, which exponentially increases the ignition delay as shown in Fig. S1.9.

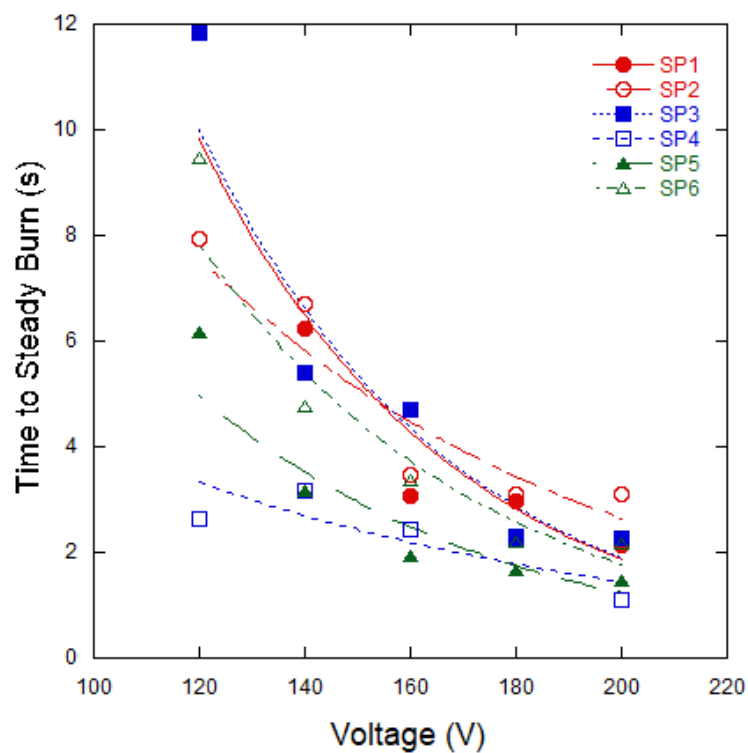


Fig. S1.8. Time to Fully Developed Flame vs Voltage

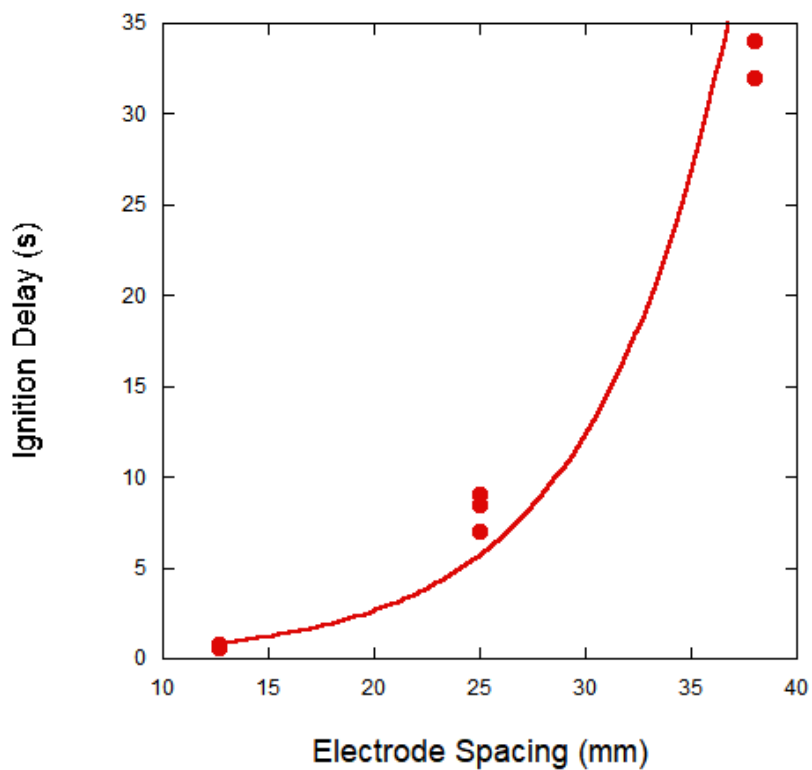


Fig. S1.9. Ignition Delay vs Electrode Spacing for SP4

S1.2.2 ECSP Resistance

Using the measurements from the impedance spectroscopy experiments, the conductivity and resistance was found for the solid phase of each ECSPs samples listed in Table S1.3. The resistance of each sample is dependent on its size, so each resistance value must be scaled to compare the melt phase and solid phase accurately. The solid phase resistance was found by converting the resistance (R) calculated using impedance spectroscopy into resistivity (ρ) using the samples cross sectional area (A) and thickness (t) (Careem, 2020).

$$\rho = \frac{R}{t/A} \quad (\text{S1.14})$$

The calculated resistivity from the impedance spectroscopy was then converted back to resistance using Eq. (S.114) and using the dimensions that the ECSPs are subjected to in the combustion experiment. Since the resistance is dependent on the amount of material, this conversion is necessary to compare the small amount of material used in the impedance spectroscopy to the larger amount of material used in the combustion experiments to make a qualitative comparison. The electrode spacing of 12.7 mm was used as the thickness (t) and the contact area between the ECSP and the electrode, 6mm by 12.7 mm, was used as the cross-sectional area (A). This conversion results in the resistance of the solid phase of the ECSPs seen in the combustion experiment prior to any decomposition occurring.

The resistance was also determined for the steady state combusting melt layer as shown in Table S1.3, which was found by dividing the applied voltage by the current draw. The resistance of the melt phase is dependent on the contact area between the electrodes which cannot be measured precisely during the composition, thus it was assumed that the contact area remained constant at 6mm by 12.7 mm. Since we cannot accurately account for possible changes in contact area, the resistances shown in Table S1.3 are meant to illustrate comparative changes in the resistance caused by the phase change from solid to liquid and across the various compositions. By comparing the resistances of the solid phase to that of the melted phase, it is clear that the solid phase is substantially more resistant to the flow of ions, but the solid phase is still conductive without the need of a preformed melt layer. This is expected, as ions can generally flow substantially easier in a liquid polymer electrolyte than in a solid polymer electrolyte (Arya, 2017). As AP is added into the solution as shown in SP4 and SP6, the resistance increases compared to SP3 and SP5 which only have LP. This can be caused by several factors such the differences in the ionic mobility of the lithium ions compared to the hydrogen ions which must first form from the ammonia ion and how good of a complex each salt forms with the PEO polymer backbone. Unlike LP, AP does not melt substantially prior to decomposition. Increasing the AP concentration increases the amount of gas in the melt layer, which would increase the melt layer resistance.

Table S1.3. ECSP Solid and Melt Phase Resistance

Sample	Average Solid Phase Resistance (ohms)	Average Resistance During Burn (ohms)
SP1	22800	91.1
SP2	25900	79.2
SP3	7600	106
SP4	8700	118.9
SP5	4800	84.5
SP6	9000	100.5

S1.2.3 Imaging of Samples

Scanning electron microscopy was used to gain an understanding on how the changing composition effects the morphology of the ECSPs. A sample of each ECSP composition was sliced into a thin wafer so the SEM could look at the morphology of the center. Each of the images obtained showed that all of the samples had some degree of surface roughness as shown in Fig. S1.10, which shows SP1 under 200x magnification. Despite the surface roughness shown in Fig. S1.10 for SP1 the overall morphology remains similar throughout the areas imaged. This suggests that the LP salt dissolved and complexed well with the PEO polymer.

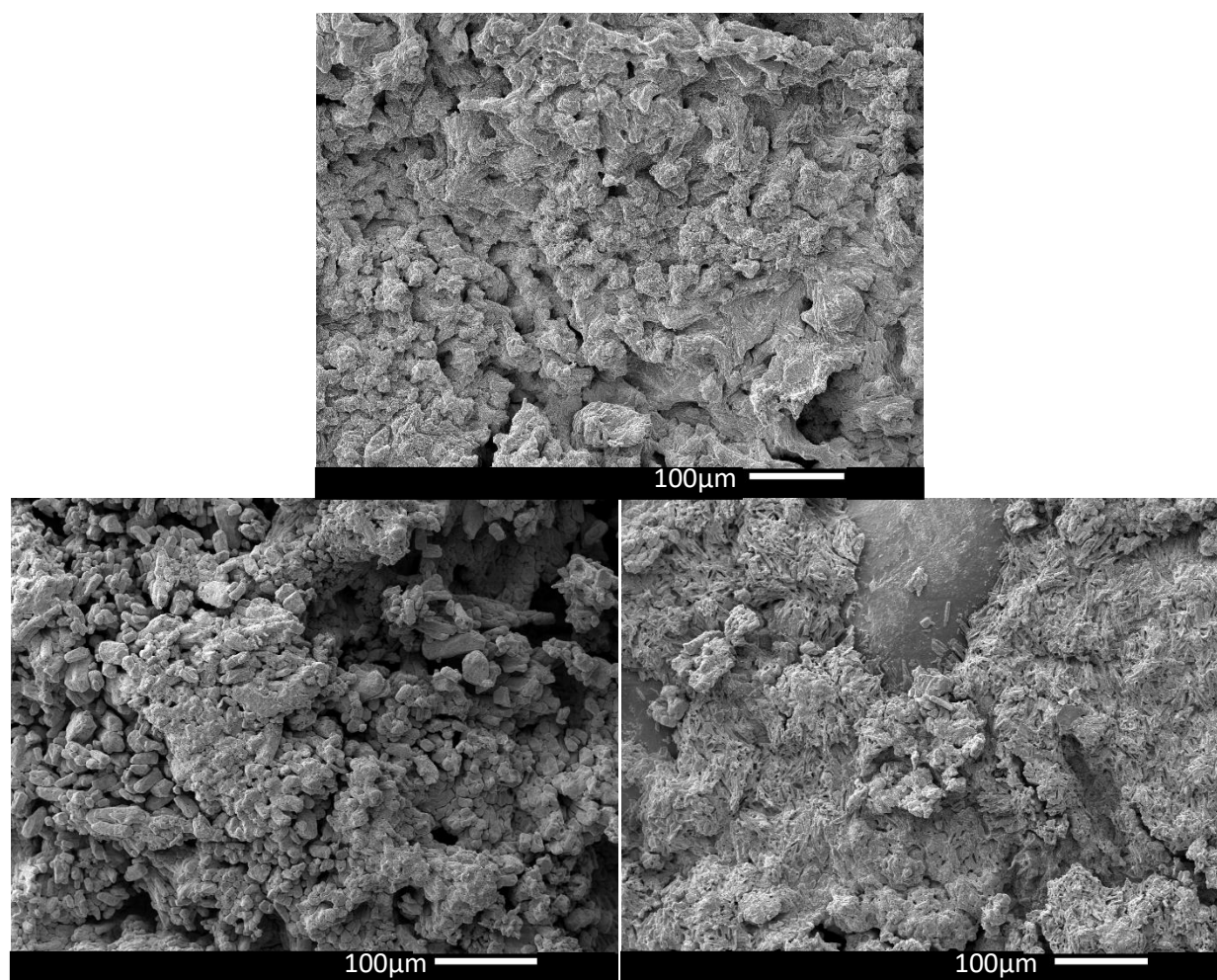


Fig. S1.10 SEM Image of SP1 (Top), SP5 (Left), SP4 (Right)

As the oxidizer salt concentration increases, the overall surface roughness begins to become rougher as shown with SP5 in Fig. S1.10. Even with the higher surface roughness in SP5, the LP was uniformly dispersed and complexed with the PEO. EDS confirmed this uniformity of LP dispersion by showing that from location to location inside of SP5, the relative amounts of LP and PEO remained nearly constant. The addition of AP, however leads to very clear changes in morphology in the ECSP as shown in the SEM image

of SP4 in Fig. S1.10. There are two clearly defined morphologies with a rough area and a smooth rounded area. Utilizing EDS, the rough area was found to be primarily LP and PEO, with small amounts of AP. Due to AP being the only nitrogen containing molecule of the added components, this smooth surface is likely a solid AP crystal that did not completely dissolve and complex with the PEO polymer. Prior imaging of AP grains has found that untreated AP can take on a round shape (Mezrovia, 2014). This lack of complexing of the larger AP crystals can explain the higher resistance seen in SP4 and SP6. The AP crystals in their pure form are highly nonconductive and having a lower complexing with the PEO would decrease the overall conductivity of the polymer electrolyte.

S1.2.4 Decomposition Cycling

To gain knowledge on the ability to create an ECSP whose combustion can be stopped and restarted, experiments were conducted during which the power was turned off to stop the electrochemical reactions and turned back on to restart the reactions. SP4 was used due to its quick response time and relatively high regression rate. Figure S1.11 shows a representative experiment where the power is initially turned on which clearly shows a change in displacement corresponding to the sample being consumed. At $t=10.5$ seconds the power is turned off, as shown by the voltage going to 0V. The displacement plot then begins to level off showing that the regression rate has slowed due to the power being removed. There is still a slight change in displacement while the power is off due to the heat from the experiment heating the sample. The residual heat partially melts the sample pushing it through the experimental apparatus. At $t=15.5$ seconds the power is turned back on as shown by the increase in voltage, and the slope of the displacement plot begins to rise again showing that the regression rate has accelerated.

From the experiments conducted, there was no time limit found that the applied power could be removed, without being able to restart the reaction with the reapplication of power. This is due to the ECSPs being conductive in their solid state, which enables the reaction to be restarted at any time. It was also found that all samples behaved in a similar manner and could be stopped and restarted easily. These experiments also show that under atmospheric conditions, the combustion reaction of the ECSP samples utilized can be stopped by the removal of the applied voltage.

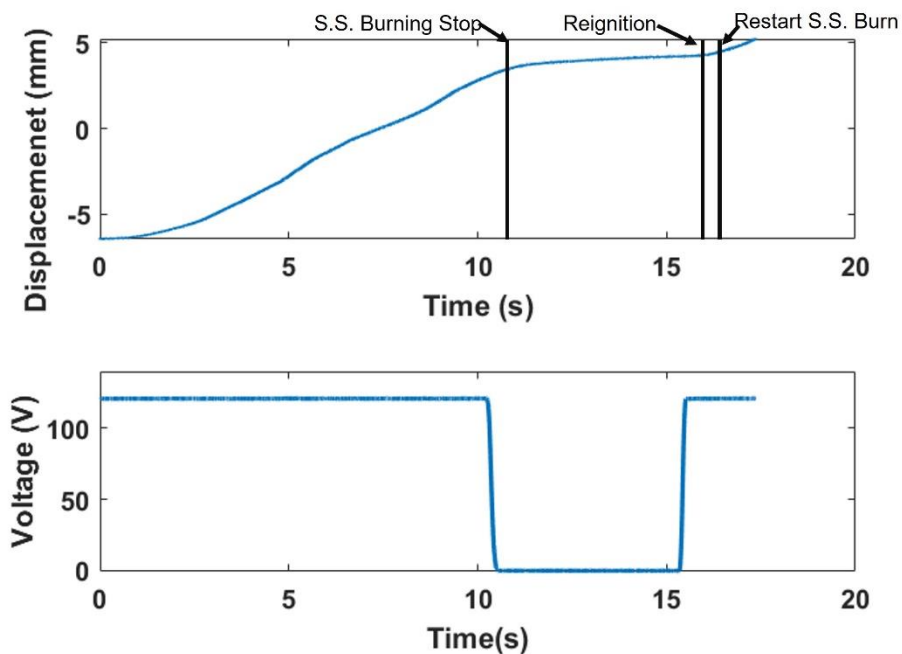


Fig. S1.11. Stopping and Restarting Combustion Through Power Cycling

S1.2 Conclusions

An experimental study was conducted on the use of ECSPs to gain an understanding on their combustion characteristics when subjected to an applied voltage potential. It was found that for all ECSP compositions used, the regression rate was highly dependent on the magnitude of the applied voltage potential. Increasing the magnitude of the applied voltage potential also greatly decreased the time required to achieve ignition and steady burning due to the increase in ionic velocity. The combustion reactions for the electrochemical decomposition were also found to vary from the standard thermal decomposition reactions. It was found that the decomposition always started with a decomposition of the PEO polymer backbone at the cathode, which created a liquid melt layer. This liquid melt layer would then spread to the anode, which would enable an accelerated decomposition of the perchlorate ions. Once the perchlorate ions started to decompose, the sample would ignite. Due to this decomposition mechanism, the spacing of the electrodes have a great effect on the time required to achieve ignition.

The composition of the ECSP was found to have a large effect on the regression rate, especially at high voltages. When AP was added in addition to LP, it was found that the regression rate versus voltage trend became nonlinear with a large increase in regression at high voltages. This is in contrast to the samples which only had LP as the oxidizer, whose regression rate followed a linear relationship with the applied voltage. This suggests that the addition of the more thermochemically energetic AP causes the decomposition to proceed at a faster rate in combination with the electrochemical decomposition. The addition of AP also changed the morphology of the ECSP, which was determined using SEM. Large AP salt crystals were found to not fully dissolve and complex completely with the PEO polymer in many cases. Regardless of the composition of the ECSPs considered in this study, it was found that the combustion

reaction could be stopped under atmospheric conditions just by the removal of the applied voltage. This shows that the combustion of the ECSPs used can be throttled by changing the magnitude of the voltage or stopped completely by its removal.

Solid Propellant Study 2 “S2”

The objective of the research outlined in this paper is to study ECSPs that are highly responsive to applied electrical power and do not require residual solvent or external heating to operate. The ionic solid oxidizer used in the ECSPs is lithium perchlorate (LP) as it has shown great potential in previous ECSPs (Gobin 2022; Gobin, 2022a; Gobin, 2022b; He, 2019). The fuel and polymer binder explored in this study is a low melting point polyethylene oxide (PEO) polymer, which was selected due to the polymer's ease of use and potential to enable the rapid creation of a conductive melt layer. Multi-walled carbon nanotubes (MWCNT) were added to the propellant to enable electrical conductivity and also act as additional fuel. Experiments were conducted to determine the ignition delay as a function of composition and applied voltage magnitude. Pressurized experiments were also conducted to characterize the impact pressure has on the burning properties of the ECSPs, and the ability to extinguish and reignite the ECSPs at various pressures and compositions.

S2.1 Methods

S2.1.1 Sample Preparation

The ECSPs were created by first measuring the required volume of acetonitrile solvent, which was purchased from Thermo Fisher Scientific and had a purity of 99.9%, into a beaker on a stir plate. The PEO polymer was then added to the beaker and allowed to stir until entirely dissolved. The PEO used in this study was purchased from Sigma-Aldrich and had a viscosity average molecular weight of 200,000 g/mol. Once the PEO was dissolved, the oxidizer LP was slowly added to the solution until entirely dissolved. The LP used in this study was purchased from Thermo Fisher Scientific and is American Chemical Society grade with a minimum purity of 95.0%. Lastly, the MWCNTs were stirred into the solution until a homogeneous solution was created. The MWCNTs were purchased from Cheap Tubes with a stated purity of over 98%, less than 1.5wt% ash, length of 10-30 μm , and an outside diameter of 10-20 nm. The beaker containing the solution was then placed inside a vacuum oven at 75°C in order to remove as much solvent as possible. The remaining solution was then cast into 12.7 x 12.7 x 25 mm molds and stored under vacuum for a minimum of two weeks to prevent absorption of atmospheric moisture and further remove residual solvent.

In our earlier research, it was discovered that some trapped solvent was required inside of the ECSPs to enable sufficient conductivity to be responsive to a voltage potential (Gobin, 2022a; Gobin, 2022b). However, if thermal input was applied to the ECSPs such that a melt layer was formed, the melt layer is sufficiently conductive to respond to the voltage potential (Khoruzhii, 2007; Khoruzhii, 2008; Gobin, 2021). In our prior study, we dried our ECSP samples in a fume hood for one week to allow the solvent to evaporate and cause the ECSP to solidify (Gobin, 2022b). When experiments using the ECSPs were conducted after the ECSPs were dried for time periods significantly longer than one week, the burning and ignition properties were affected (Gobin, 2022b). The addition of MWCNTs into the ECSPs is to enable more consistent combustion properties in the ECSPs regardless of the drying time.

The compositions of the ECSPs used in this study are listed in Table S2.1. The lower bound of MWCNT concentration was selected as below 2.5 wt% MWCNT the ECSPs did not consistently ignite when a

voltage potential was applied. The upper bound of 5.0 wt% MWCNTs was selected since higher concentrations of MWCNTs makes casting the solution difficult. The midpoint between the upper and lower bounds (3.75 wt% MWCNT) was selected as the third composition. However, after running several experiments exploring the ignition delay of the ECSPs it was observed that the ECSP_3.75 and ECSP_5 compositions had very similar ignition delays whereas the ECSP_2.5 and ECSP_3.75 compositions had a very large difference in their ignition delays. Due to this observed trend in the ignition delay with respect to composition, a fourth composition was selected which had 3.13 wt% MWCNTs, which is the midpoint between the ECSP_2.5 and ECSP_3.75. The percent PEO polymer was held fixed as going much lower than 25 wt% PEO results in an ECSP that had poor mechanical properties. The theoretical specific impulse and flame temperature for the ECSP compositions used in this study was calculated using the NASA Chemical Equilibrium with Applications (CEA) program (Gordon, 1994) as shown in Fig. S2.1. The CEA program was set in the rocket equilibrium configuration with a chamber pressure of 6.9 MPa and expanded to sea level. When no MWCNTs are added, the composition is at peak theoretical performance, and as MWCNTs are added and the oxidizer is removed, the composition becomes more fuel rich and the performance decreases. However, in order to create a responsive propellant, additives such as MWCNTs must be used. The intention of the addition of MWCNTs is to alter the ignition mechanism from mainly electrochemical to a combined thermal/electrochemical mechanism.

Table S2.1 ECSP composition

Sample Name	Percent Polymer	Percent LP	Percent MWCNT
ECSP_0	25	75	0
ECSP_2.5	25	72.5	2.5
ECSP_3.13	25	71.87	3.13
ECSP_3.75	25	71.25	3.75
ECSP_5	25	70	5.0

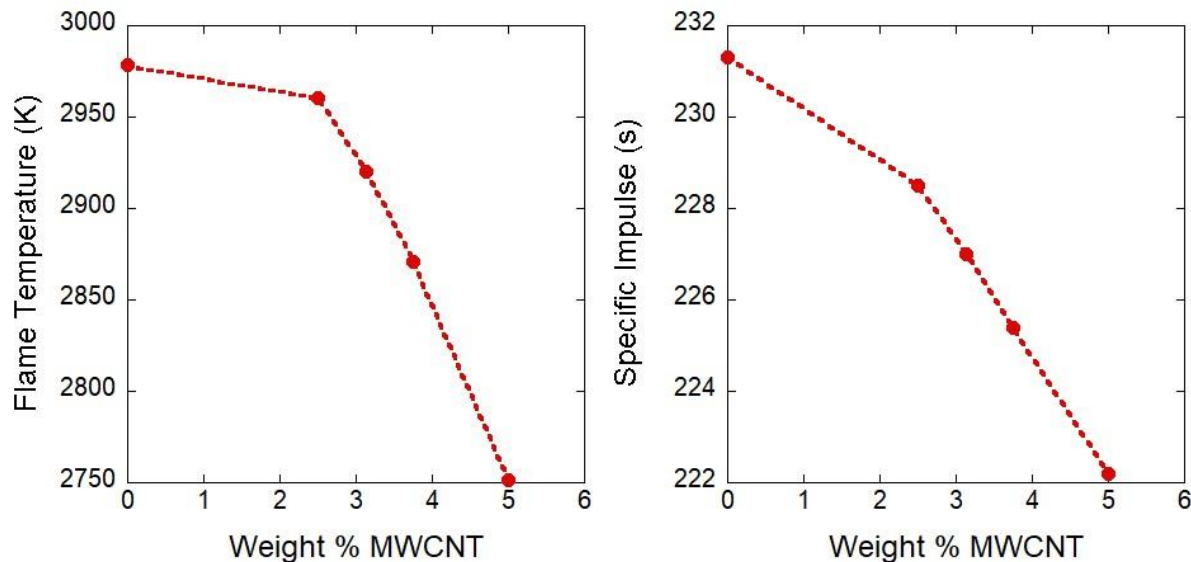


Fig. S2.1 Flame temperature (left) and specific impulse (right) versus weight percent MWCNT

S.2.1.2 ECSP Material Characterization

To gain insight into the thermal response of the ECSPs of interest in this study, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were conducted. A Netzsch STA 449 F5 Jupiter simultaneous thermal analyzer was used to carry out the thermal analysis. Initial thermal decomposition experiments were conducted under a nitrogen environment from 25°C to 800°C with a heating rate of 10°C per minute. Certain nanomaterials such as MWCNTs exhibit a catalytic impact on the decomposition of certain oxidizers such as ammonium nitrate and ammonium perchlorate (Miyake, 2010; Vara, 2019). To verify if MWCNTs catalyze the decomposition of LP additional DSC experiments were conducted at heating rates varying from 2.5°C to 30°C per minute on LP and LP mixed with MWCNTs. Using the Kissinger method (Kissinger, 1956), the activation energy was determined for both compositions to determine the catalytic impact of the MWCNTs. To briefly summarize the Kissinger method for determining the kinetics of materials, the temperature of the peak reaction rate (T_p) is first determined for a range of heating rates (β) (Kissinger, 1956). Then using the relationship developed by Kissinger shown in Eqn. S2.1, the activation energy used in the Arrhenius rate equation (E) can be determined using the peak reaction rate temperature, heating rate, and the gas constant (R) (Kissinger, 1957).

$$\frac{d\left(\ln\frac{\beta}{T_p^2}\right)}{d\left(\frac{1}{T_p}\right)} = -\frac{E}{R} \quad (\text{S2.1})$$

Since the MWCNT composition of the ECSPs was varied, electrical conductivity experiments were conducted to highlight the contribution of MWCNTs on the conductivity properties of the ECSPs in this study. Using two parallel plate graphite electrodes, the conductivity was determined using an Autolab PGSTAT302N. The ECSP sample of interest was placed in between the electrodes and the conductivity was measured using an AC voltage sweep similar to our prior studies (Gobin, 2022a; Gobin, 2022b).

S2.1.3 Ignition Delay Experiments

The ignition delay of each propellant composition was characterized as a function of applied voltage by a series of experiments that were conducted at atmospheric pressures similar to our prior work (Gobin, 2022a; Gobin, 2022b). Briefly, the ECSP of interest was loaded into the ceramic experimental apparatus as shown in Fig. S2.2. The apparatus comprises an electrically isolating ceramic base which was used to contain the experiment, and two 6 x 12.7 mm copper plate electrodes that were placed on the sides of the ECSPs which allow the voltage potential to be applied across a sample. A predetermined voltage was applied using an XP Power HPT5K0-L DC power supply. The voltage was measured and recorded during the experiment using a step-down circuit and a National Instruments SCB-68A mass terminal and USB-6363 data acquisition unit (DAQ). The ignition delay and decomposition characteristics of the ECSP were determined by high-speed cinematography using a Vision Research Phantom VEO 7.10L high-speed camera. Ignition was defined as the first observable light preceding a large luminous flame. Using the time between when the voltage is applied and the sign of first light, the ignition delay can be determined for each ECSP composition for a range of voltages. Additional experiments were conducted using a similar configuration to that shown in Fig. S2.2 with the exception that the spacing between the electrodes was increased to 16.9 and 21.2 mm to analyze the impact that electrode spacing has on the ignition delay.

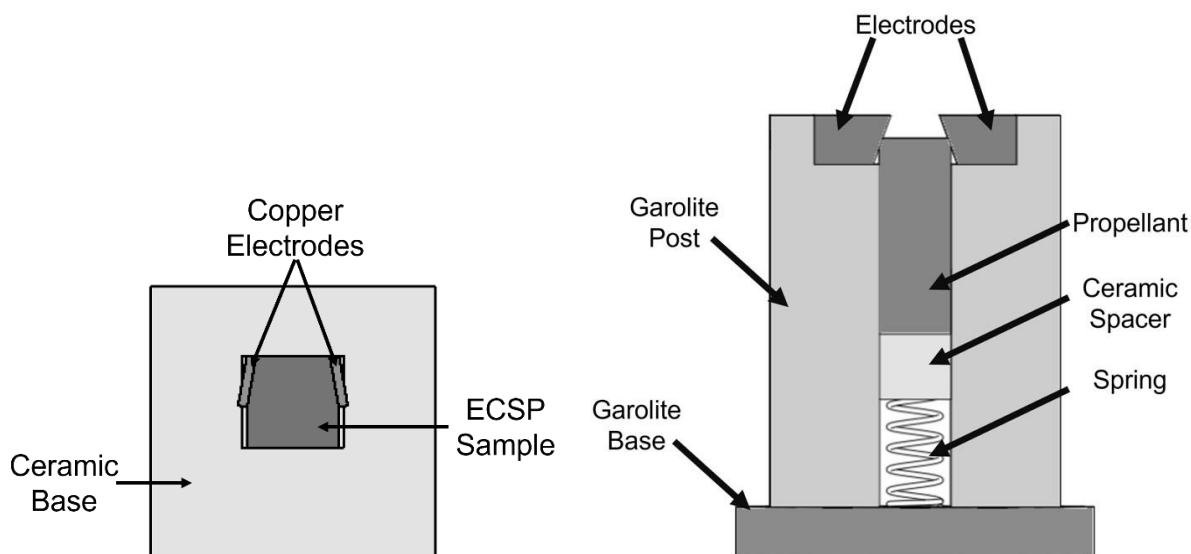


Fig. S2.2 Ignition delay experimental apparatus (left) and electrically isolated experimental apparatus (right)

S2.1.4 Electrochemical Decomposition and Combustion Characteristics

To obtain more detailed imaging of the decomposition process and the flame structure during combustion, a new electrically isolated experimental combustion apparatus was developed as shown in Fig. S2.2. This apparatus comprises two electrically isolating garolite posts on top of which two stainless steel electrodes were placed. Stainless steel electrodes were utilized as copper electrodes were found to slightly melt when subjected to the temperatures experienced during pressurized combustion experiments. The ECSP sample was placed between the garolite posts and pushed into the electrodes using a spring, which ensured that the

ECSP sample had sufficient contact with the electrodes and new ECSP was continuously fed into the electrodes as it is consumed. The voltage was applied, measured, and recorded using the same procedure as discussed in Section II.C.1. The resulting current draw was measured using a Teledyne T3CP100-2 current probe and recorded using the DAQ. In addition to using the Vision Research Phantom VEO 7.10L high-speed camera a FLIR X6981 mid-wave infrared camera was utilized to record the temperature of the propellant surface leading up to ignition. The infrared camera was equipped to record temperatures between 10°C and 350°C and the temperature analysis was conducted using the FLIR Research Studio software.

S2.1.5 Laser Assisted Combustion

During the combustion process, when voltage is applied using the electrodes, electrochemical decomposition is occurring in addition to ohmic heating due to the movement of ions and electrons through the propellant. To verify that the increased regression rate observed in the propellants is not solely due to ohmic heating of the propellant a set of experiments was conducted in which a laser was used to ignite the propellant and sustain combustion. This allows the application of a known heat flux into the propellant to compare against the ohmic heat generated during the combustion process using the electrodes and an applied voltage. The laser used in this study was a Coherent Inc. Diamond J-2 CO₂ laser with a 10.6 μm wavelength beam. Preliminary experiments in which the surface of the ECSPs was ignited with the laser resulted in a 5 mm circle where the propellant burned and all material outside of that circle did not react. As such, the ECSP samples used in this study were 5mm diameter cylinders and the laser beam was directed perpendicular to the top surface of the cylinder. During the decomposition and combustion process, the VEO 7.10L high-speed camera was used to record the experiment and allow for the determination of the linear regression rate of the propellant during steady laser-assisted combustion.

S2.1.6 Pressurized Combustion Experiments

Combustion experiments were conducted at elevated pressure in an optically accessible strand burner to determine pressure deflagration limits and sensitivity of the burning rate to both pressure and voltage. The ECSP of interest was placed into the same experimental apparatus used for the atmospheric experiments as shown in Fig. S2.2. The entire apparatus shown in Fig. S2.2 was then loaded into the optically accessible strand burner as shown in Fig. S2.3 and the experiments were conducted. The strand burner was pressurized to a predetermined pressure using a nitrogen gas purge and a predetermined voltage was applied across the ECSP using an XP Power HPT5K0-L DC power supply. Regression rates of the ECSPs were determined by using video recording to track the displacement of the propellant over the course of the experiment. The base of the ceramic spacer was tracked in order to determine the burning rates. Additional experiments were carried out at various pressures where the electrical power was turned off to determine the ability to extinguish the ECSPs at elevated pressures.

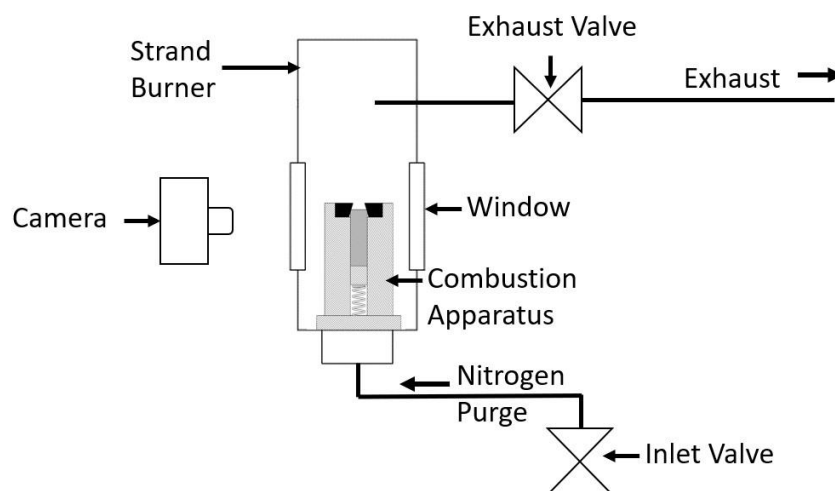


Fig. S2.3 Optically accessible strand burner schematic

S2.2 Results

S2.2.1 ECSP Material Characterization

The results of the TGA and DSC for the LP and PEO used in creating the ECSPs used in this study are shown in Fig. S2.4. The PEO melts at around 65°C as shown by the endotherm, and thermally decomposes at 350 °C. The LP melts at around 250°C but does not experience any decomposition and mass loss until 480°C as shown in Fig. S2.4. The mass loss is exothermic and is due to the lithium perchlorate decomposing into lithium chloride and gaseous oxygen (Marvin, 1945). The endotherm occurring in LP at 606°C is caused by the melting of lithium chloride (Kamali, 2011). The final mass loss that gradually begins at 696°C is due to the evaporation of the remaining lithium chloride. The MWCNTs are not expected to decompose significantly in a nitrogen environment as was used in our study. Earlier studies have found that slight decomposition of MWCNTs does not occur until around 480°C due to the degradation of the graphene walls (Zhang, 2017; Darwish, 2014). The gradual decomposition continues until around 830°C with around 90% of the original weight of the MWCNTs remaining (Shanmugharaj, 2007; Okpalugo, 2005).

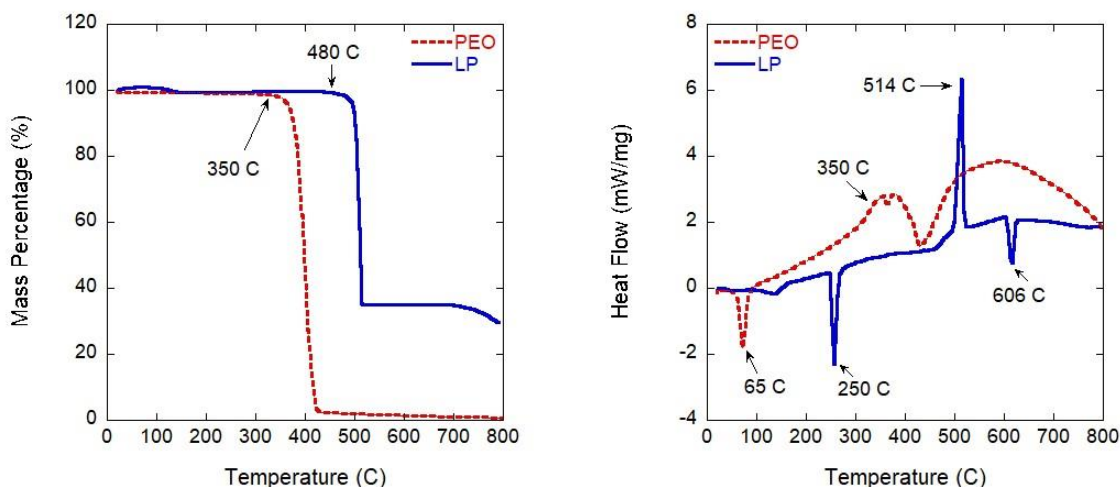


Fig. S2.4 TGA (left) and DSC (right) results of PEO and LP

The results of the TGA and DSC experiments for the ECSPs compositions are shown in Fig. S2.5. For ease of visualization only select ECSP compositions are shown in Fig. S2.5, however all DSC plots for the ECSP compositions are provided in Appendix A. Each of the ECSP compositions had 10-20% mass loss at low temperatures due to solvent evaporation despite being stored for extended periods of time at elevated temperatures and vacuum conditions. In our prior research using similar compositions to this study, we observed that the concentration of trapped solvent was also around 10-20% when dried under a fume hood for a shorter time (Gobin, 2022b). Due to sourcing problems, the LP used in this study differs from those used in our prior studies (Gobin, 2021; Gobin, 2022; Gobin, 2022b) and seemingly traps more solvent. Despite having similar solvent concentrations, the ECSPs used in our prior studies were tacky/sticky whereas the ECSPs in this study were dry to the touch throughout the ECSP (Gobin, 2022a). Acetonitrile has a boiling point of 82°C at atmospheric pressures (O'Donnell, 1965), which closely matches the low-temperature endotherm observed in the DSC plots and initial mass loss in the TGA plots in Fig. S2.5. However, the mass loss continues steadily until approximately 150°C for all ECSP compositions. The continued mass loss can be attributed to the interaction that lithium salts, such as LP, have with solvents (Denney, 2022; Xuan, 2004; Foran, 2020). With acetonitrile, the nitrogen atom in the cyanide functional group ($C \equiv N$) interacts with the lithium ions, which causes a structural change in the acetonitrile (Xuan, 2004). This association between the acetonitrile and the lithium ions results in the acetonitrile not entirely evaporating until around 160°C (Denney, 2022; Commarieu, 2019), which closely matches the observed trends in the TGA plots in Fig. S2.5. To confirm whether this interaction between LP and acetonitrile was the cause of the mass loss at low temperatures an additional TGA experiment was conducted considering only LP which was initially dissolved in acetonitrile. For this experiment, LP was dissolved in acetonitrile and then dried under vacuum conditions at room temperature. TGA analysis was then run on the dried powder using a nitrogen environment with a heating rate of 10°C per minute. Figure S2.6 shows the results of this experiment, and a significant mass loss is observed which is not observed in the pure LP. This shows that the interaction between LP and acetonitrile is significant and explains why large amounts of the solvent remain in the ECSPs. The elevated evaporation temperature is also observed when water interacts with LP creating hydrated lithium perchlorate or lithium perchlorate trihydrate (Markowitz, 1960). In lithium

perchlorate trihydrate, the water does not completely evaporate until temperatures are well above the boiling point of water (Markowitz, 1960). Due to the hygroscopic nature of the ECSPs used in this study, this potential formation of lithium perchlorate trihydrate can further exacerbate the mass loss at temperatures between 100°C and 200°C.

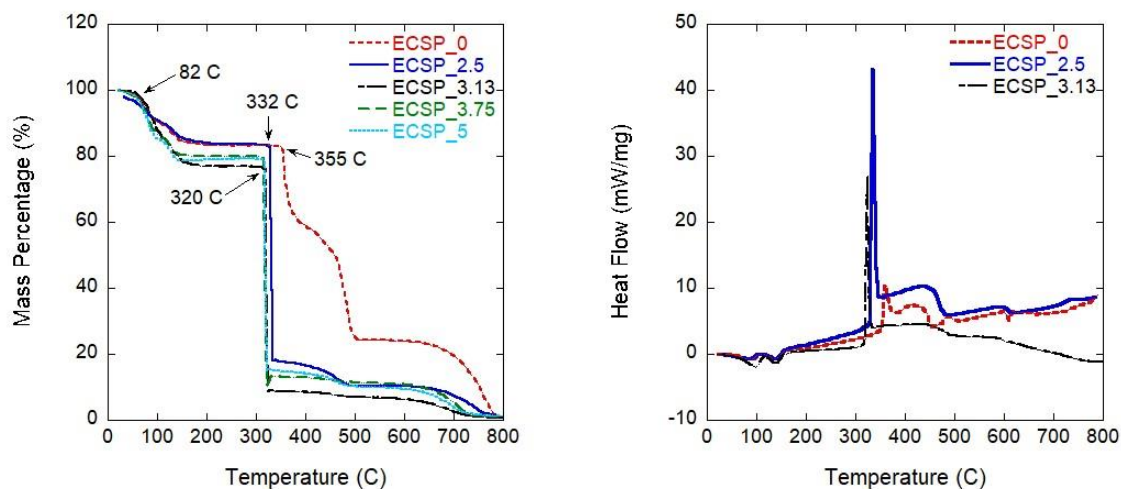


Fig. S2.5 TGA (left) and DSC (right) results of ECSP compositions

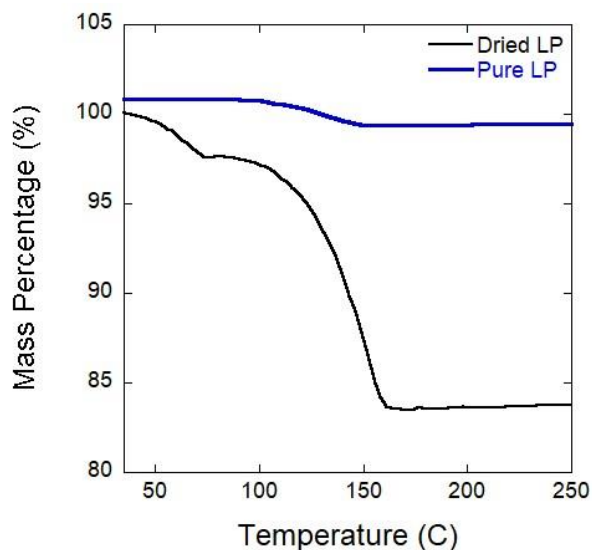


Fig. S2.6 TGA results of dried LP after dissolving in acetonitrile and pure LP

The primary mass loss occurs at 320°C for ECSP_3.13, ECSP_3.75, and ECSP_5, whereas ECSP_2.5 and ECSP_0 experience their mass loss at 332°C and 355°C respectively as shown in Fig. S2.5. This mass loss corresponds to the large exotherm shown in Fig. S2.5 and shows that this mass loss is due to thermal runaway of the ECSP. The mass loss for the ECSPs containing nanotubes occurs significantly faster with a nearly vertical drop in the mass, whereas ECSP_0 has a gradual two-step mass loss. The change in the decomposition characteristics due to the addition of the MWCNTs may be caused by the catalytic nature of carbon nanotubes on the decomposition characteristics of certain propellants (Vara, 2019). One example of

the catalytic impact of MWCNTs is in the decomposition of ammonium perchlorate. The addition of MWCNTs causes the two-step decomposition of AP to become a single-step decomposition with a more rapid mass loss (Tavakoli, 2022).

To verify the catalytic impact of MWCNTs on LP, the Kissinger method (Kissinger, 1956; Kissinger, 1957) was utilized to determine the activation energy of LP dissolved in acetonitrile and then LP dissolved in acetonitrile with 5wt% MWCNTs added. Figure S2.7 shows the TGA and DSC results of the LP compared to the LP/MWCNT mixture and clearly shows that the addition of the MWCNTs decreases the temperature of the start of the primary mass from 480°C to 336°C and decreases the temperature of peak reaction rate from 507°C to 378°C when the samples are heated at 10°C per minute in a nitrogen environment. Taking the peak reactivity temperature at various heating rates for each mixture allows the creation of a Kissinger plot as shown in Fig. S2.8. As shown in Eqn. 1, the slope of the lines in Fig. S2.8 is the negative of the activation energy divided by the gas constant. The activation energy for the LP after being dissolved in acetonitrile was found to be 193kJ/mol, whereas the LP mixed with the MWCNTs had an activation energy of 148kJ/mol. Reported values on the activation energy of the decomposition of LP range from 168kJ/mol to 218kJ/mol (Cordes, 1974; Markowitz, 1961) which agrees with the activation energy of LP calculated in this study. This confirms that the MWCNTs have a catalytic impact on the LP which decreases the temperature at which the decomposition of LP takes place and also decreases the activation energy to initiate thermal decomposition.

The electrical conductivity of each of the ECSP compositions was also determined as shown in Table S2.2. As expected, as the concentration of MWCNTs is increased, the conductivity of the ECSPs increased due to the high electrical conductivity of the MWCNTs. ECSP_0 has a very low conductivity; however, the conductivity increases by over two orders of magnitude when 2.5 wt% MWCNTs are added to the propellant as in ECSP_2.5. There is a slight increase in conductivity when the MWCNT concentration is further increased to ECSP_3.13, and a significant increase occurs when the MWCNT concentration is further increased to ECSP_3.75. Increasing the MWCNT content further to ECSP_5 continues to increase the conductivity but not as significantly. The conductivity of the MWCNT-based ECSPs in this study was lower than the ECSPs used in our prior studies which had a conductivity of the order of magnitude of approximately 1×10^{-2} S/m (Gobin, 2022b). However, the conductivity of the previous ECSPs slowly decreased as the excess solvent evaporates, which is not the case in the ECSPs that utilize MWCNTs.

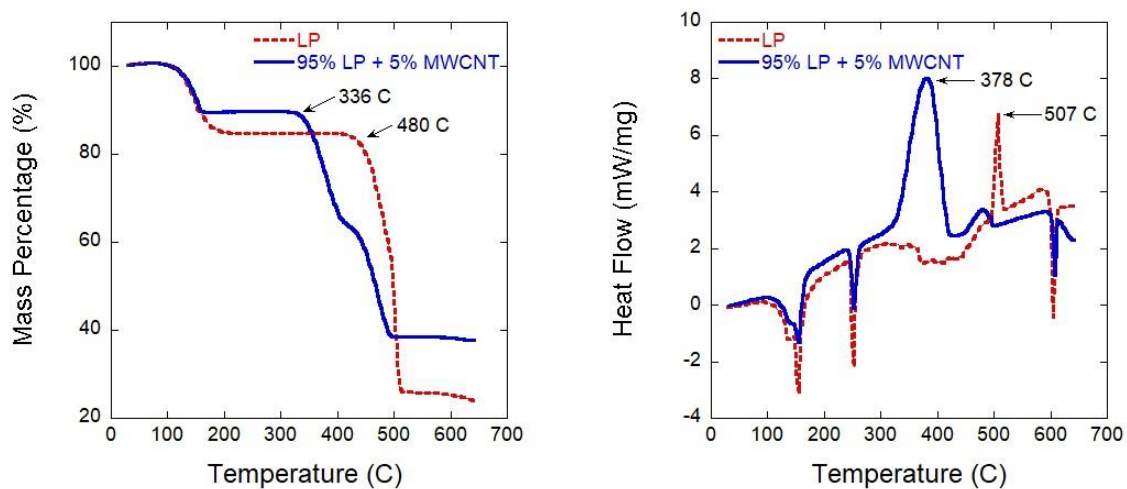


Fig. S2.7 TGA (left) and DSC (right) results of LP and 95% LP + 5% MWCNT at a heating rate of 10°C per minute

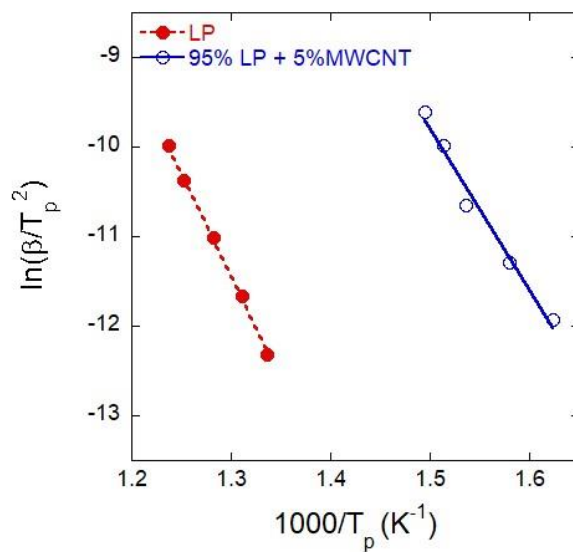


Fig. S2.8 Kissinger plot of LP and 95% LP + 5% MWCNT

Table S2.2 ECSP conductivity

Sample Name	Conductivity (S/m)
ECSP_0	1.9×10^{-12}
ECSP_2.5	3.4×10^{-10}
ECSP_3.13	4.9×10^{-10}
ECSP_3.75	1.4×10^{-8}
ECSP_5	2.2×10^{-8}

S2.2.2 ECSP Ignition Delay

To verify that the addition of MWCNTs enables sufficient electrical conductivity to melt the ECSPs through ohmic heating an initial study was conducted where paraffin wax was used with LP and MWCNTs. The paraffin wax was melted and combined with the LP and MWCNTs and cast into 12.7 x 12.7 x 25 mm molds and stored inside a vacuum oven to prevent absorption of atmospheric moisture. In previous research, it has been proven that pure paraffin wax in both its solid and molten form does not exhibit electrochemical properties and does not respond to an applied voltage potential using electrodes (Zamir, 2017). However, once ionic salts were placed inside of the paraffin wax melt layer, a small amount of ionic conductivity was achieved through the melt layer (Zamir, 2017). As such, paraffin was selected as an initial binder to verify that the use of MWCNTs enables the creation of a melt layer such that ionic conductivity can be achieved which leads to ignition. Since no solvent was used in the creation of the paraffin wax-based ECSPs, this preliminary study also verifies that the use of MWCNTs enables the creation of ECSPs that do not need trapped solvent to ignite when voltage is applied. In these preliminary studies, it was discovered that compositions above 2.5% weight MWCNTs readily melt and ignite when subjected to a voltage potential from two electrodes but did not quench when the power was removed even under atmospheric conditions. An ECSP composition comprising 25 wt% paraffin, 70 wt% LP, and 5 wt% MWCNT ignites in 0.73 seconds on average when 120V was applied but continued to burn when the power was turned off. This demonstrated that the use of MWCNTs enables the creation of ECSPs that can ignite independent of solvent concentration and was used as a starting point for the composition of ECSPs used in this study.

When the voltage potential was applied to ECSPs, the formation of a melt layer was observed followed shortly by ignition. In this study, ignition was defined as the first observable light preceding full combustion as shown in Fig. S2.9. For every composition of ECSP containing MWCNTs considered in this study, a decrease in the ignition delay was observed as the voltage potential increased as shown in Fig. S2.10. When no MWCNTs are added to the ECSP as is the case in ECSP_0, no ignition or decomposition was achieved. The concentration of trapped solvent was not high enough to ignite ECSP_0 when the voltage was applied even though the ECSPs used in our earlier studies had a similar composition and trapped solvent amount (Gobin, 2022b), further illustrating how changing the LP supplier changes the properties of the ECSPs. Each point in Fig. S2.10 is an average of three experiments and the error bars signify the standard deviation. In the case of ECSP_2.5, ignition was not consistently achieved at voltages below 160V, even when the power was applied for over one minute. The ECSP_3.75 and ECSP_5 have very similar ignition delays and were much quicker to ignite compared to the other compositions. The decrease in the ignition delay closely follows the increase in conductivity of the ECSPs shown in Table S2.2 in Section S2.2.1 Both ECSP_3.75

and ECSP_5 have significantly shorter ignition delays than similar ECSP compositions that utilize trapped solvent alone to be conductive and do not have any added MWCNTs (Gobin, 2022b), which illustrates how beneficial the MWCNTs are to lowering the ignition delay. More importantly, the MWCNT-based ECSPs consistently ignited with a similar delay regardless of the amount of time they were allowed to age under vacuum conditions which was not the case with ECSPs dependent on solvent alone (Gobin, 2022b).



Fig. S2.9 ECSP with MWCNTs at initial state (left) and at ignition (right)

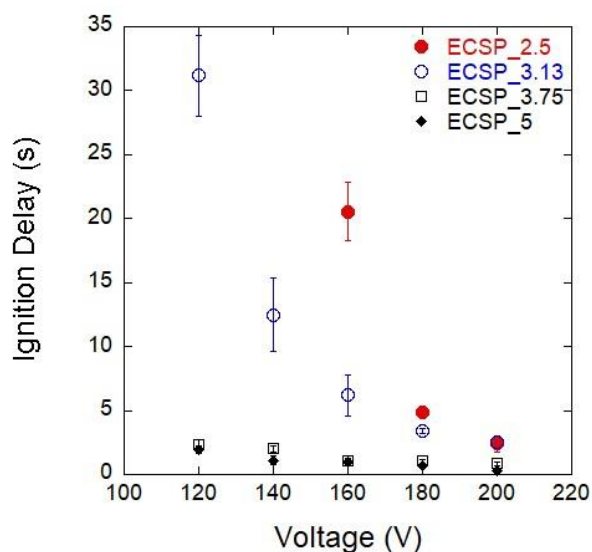


Fig. S2.10 Ignition delay of ECSPs versus the applied voltage potential

ECSP_3.75 was selected for additional experiments to explore the impact electrode spacing has on the ignition delay when the voltage is held constant. It was discovered that as the electrode spacing is increased and the voltage is held constant, the ignition delay increased linearly as shown in Fig. S2.11. Each data point in Fig. S2.11 is an average of three experiments and the error bars signify the standard deviation in the experiments at each condition. The linear increase in the ignition delay is in contrast to prior studies on ECSPs without MWCNTs which exhibited a nonlinear increase in ignition delay with increasing electrode spacing (Gobin, 2022b), further highlighting the contributions of the MWCNTs. The proposed reason for the change in the relationship between the electrode spacing and the ignition delay is due to the change in

the initial decomposition mechanism of the ECSPs. In our previous work on similar ECSPs which did not have any MWCNTs in the compositions the melt layer clearly began forming at the cathode and moved toward the anode (Gobin, 2022b). When no MWCNTs are used in the ECSPs, the melt layer forming at the cathode is due to a known instability of PEO at the cathode when exposed to high voltages which causes chain scission of the PEO backbone (Gobin, 2022b; Prosini, 1998; Simonetti, 2017)). The formation of the melt layer at both electrodes in the ECSPs when the MWCNTs are added is proposed to be caused by the ohmic heating that is occurring due to the electrical conductivity that is now present. This ohmic heating creates the melt layer, which increases the ionic conductivity to the point that ignition of the ECSPs is achieved. The linear increase in the ignition delay observed in Fig. S2.11 as the electrode spacing increases is due to the ohmic heating being the driving factor creating the melt layer. The heat generated by the electrical current increases as the current flow increases. Due to resistance (R) being related to the material property of conductivity (σ), cross-sectional area (A), and separation distance (L) as shown in Eqn. S2.2 as the separation distance increases the resistance also increases. The linear increase in resistance as the separation distance increases also linearly decreases the current flow through the ECSP which causes less heat to be generated and a slower formation of the ion conductive melt layer.

$$R = \frac{L}{\sigma A} \quad (\text{S2.2})$$

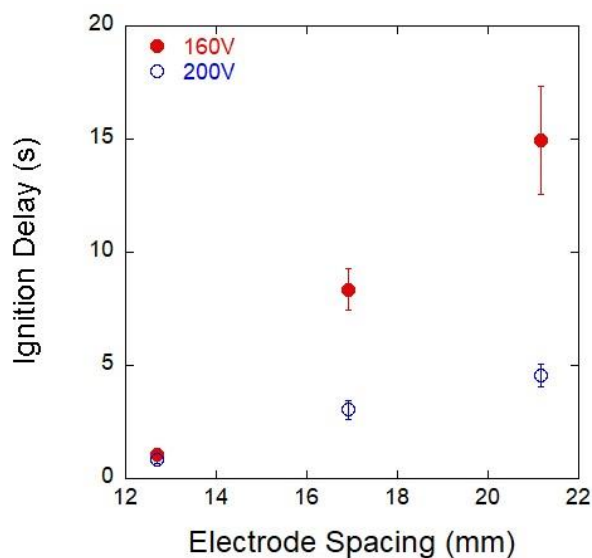


Fig. S2.11 ECSP_3.75 ignition delay with varying electrode spacing

S2.2.3 Electrochemical Decomposition and Combustion Characteristics

The application of a voltage potential to the ECSPs which contain MWCNTs triggers the formation of a melt/decomposition layer that starts at both electrodes with a slight favoring of the cathode as shown in Fig. S2.12. The time $t=0$ seconds in Fig. S2.12 corresponds to the time when the voltage application is applied. The melt layer grows from each electrode until connecting in the middle of the propellant where it then grows in size as shown at time $t=3.9$ seconds in Fig. S2.12. Ignition was observed to always occur at the anode in the ECSPs which contain MWCNTs and shortly after ignition, the entire surface of the propellant in between the electrodes combusted.

Due to ECSP_0 not being conductive in its solid state, the application of a voltage potential does not trigger decomposition or ignition. In order to ignite ECSP_0, a conductive medium must be placed across the top surface of the propellant in between the electrodes to increase the conductivity of the top surface to the point that the propellant can decompose. In this study, a drop of water was placed on the top surface of the ECSP_0 composition in between the electrodes. When the voltage was applied the top surface decomposed and ignited. Once combustion was achieved and a conductive melt layer was formed, the rest of the propellant burned through the application of the voltage potential alone. An example of the decomposition and combustion process of ECSP_0 is shown in Fig. S2.13, where the time $t=0$ seconds corresponds to the time at which the voltage potential is applied. The formation of the melt/decomposition layer was observed to start exclusively at the cathode and then grow towards the anode, similar to prior studies with a similar composition (Gobin, 2022b). Once the melt layer reaches the anode, the melt layer grows very large as shown at time $t=33.4$ seconds in Fig. S2.13. Ignition was observed to always occur at the anode regardless of the applied voltage magnitude. The flame then grew from the anode to the cathode as shown at time $t=34.2$ seconds before becoming fully developed and reaching a steady state. To further show the flame structure in ECSP_0 additional experiments were conducted where

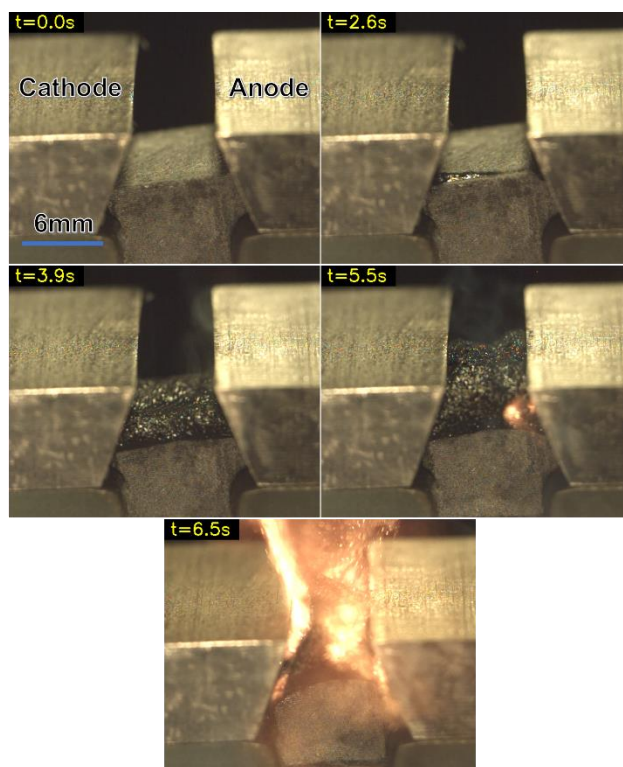


Fig. S2.12 ECSP_3.75 decomposition and ignition with 160V

the lighting of the propellant was removed to allow the flame to illuminate the propellant surface as shown in Fig. S2.14. In Fig. S2.14 the time $t=0$ seconds does not correspond to the power being applied and is used as a reference point for the following images in the sequence. The electrodes are outlined to provide a reference for the location of the flame development. In these images, the flame clearly starts at the anode and then grows towards the cathode before becoming fully developed. The fully developed flame also is observed to be very close to the surface of the propellant.

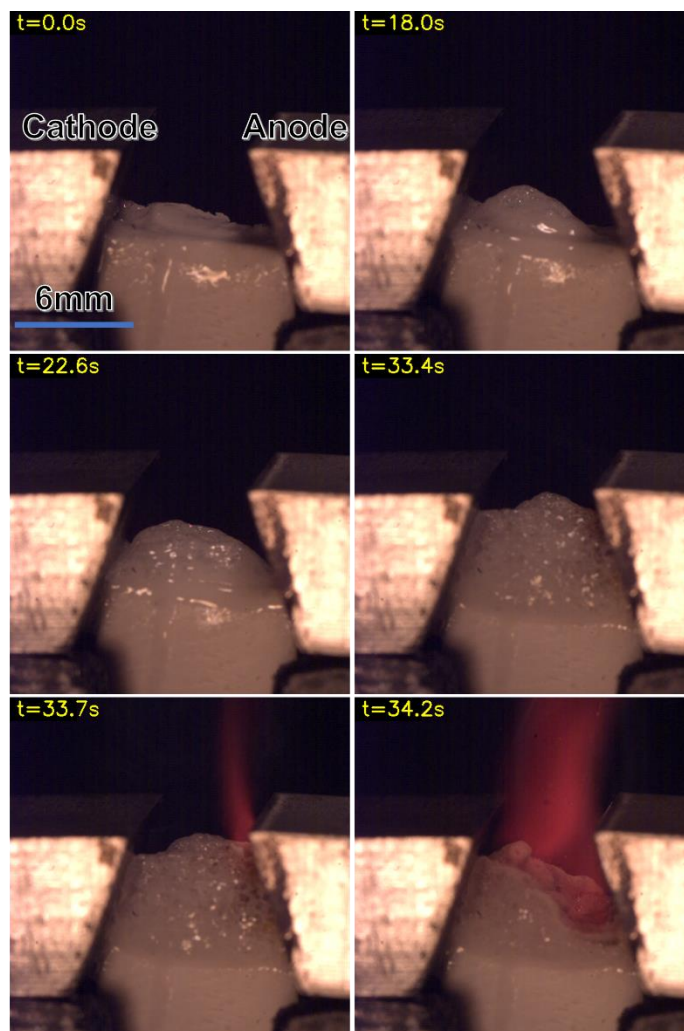


Fig. S2.13 ECSP_0 decomposition and ignition with 200V

Tracking the surface temperature of the propellants using the factory-calibrated FLIR X6981 infrared camera resulted in the observation that the surface of the propellants does not heat up uniformly. The emissivity of the ECSPs is unknown therefore the temperature values illustrate a general trend and are not exact values. Recording the temperature of the propellant next to the anode compared to the temperature of the propellant next to the cathode showed that for both ECSP_3.75 and ECSP_0, the temperature rises more initially at the anode than the cathode as shown in Fig. S2.15. The time $t=0$ seconds in Fig. S2.15 does not correspond to the time when voltage is applied and is intended only as a reference. Due to the addition of a drop of water to increase conductivity and the use of higher voltage, the ECSP_0 temperature rise happens more rapidly than the ECSP_3.75 composition in Fig. S2.15. The more rapid temperature rise at the anode is likely due to the electrochemical reactions taking place at the anode. The oxidizing perchlorate ions are expected to move to the anode where they can decompose and react with the polymer binder. Further evidence of the significant electrochemical reactions occurring at the anode is that the ignition of the ECSPs was observed to always occur at the anode. This illustrates that the reactions occurring at the anode likely release more heat and drive the overall ignition of the ECSPs.

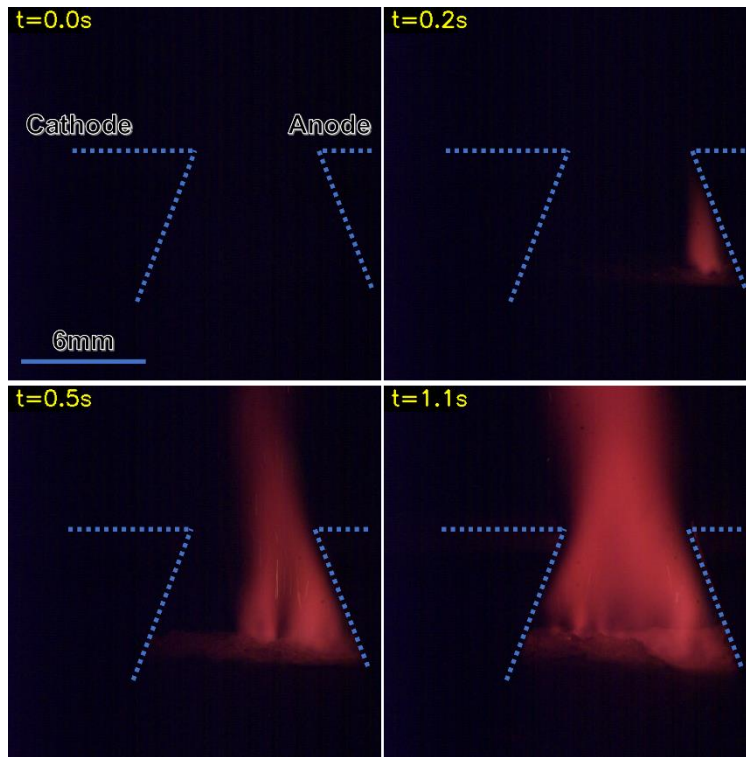


Fig. S2.14 ECSP_0 flame structure at 200V and atmospheric conditions

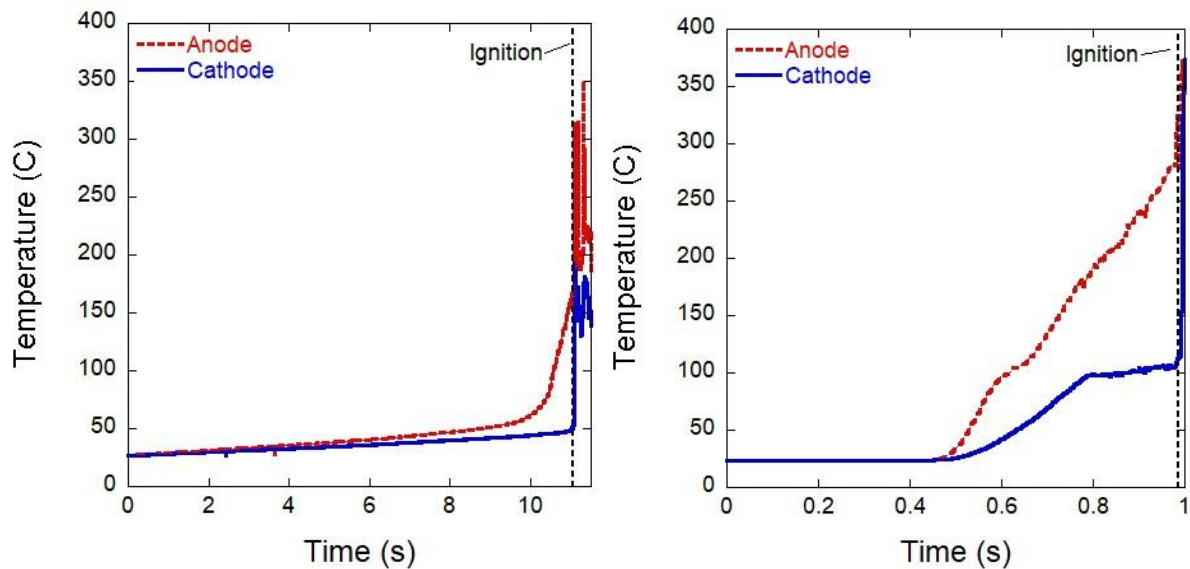


Fig. S2.15 Propellant surface temperature of ECSP_3.75 at 160V (left) and ECSP_0 at 180V (right)

S2.2.4 Laser Assisted Combustion

The use of the laser to decompose the propellant allows for a known heat flux to be applied to the surface of the propellant to analyze how the applied electrical power compares to a similar thermal power. Figure S2.16 shows the ignition and combustion process when 0.7W/mm^2 is applied to ECSP_0 with the time $t=0$

seconds corresponding to the time when the laser is turned on. ECSP_0 ignited at time $t=0.41$ seconds and achieved a fully developed flame at 0.6 seconds. Once the fully developed flame is formed and the laser is kept on, the propellant will then combust, and the linear regression rate can be determined. The resulting linear regression rate as a function of applied heat flux is shown in Fig. S2.17 for ECSP_0 and ECSP_3.75. Each data point for the laser-assisted regression rate in Fig. S2.17 is an average of 3-4 data points with the error bars signifying the standard deviation. ECSP_3.75 has an overall higher regression rate compared to ECSP_0 across all of the heat flux conditions analyzed. This is potentially due to the higher thermal conductivity the MWCNTs add to the propellant or the catalytic impact of the MWCNTs.

Due to the unknown absorption efficiencies of the propellants, the heat flux values in Fig. S2.17 are the heat being applied to the surface, not the heat absorbed by the surface. Studies on the laser ignition of AP and hydroxyl-terminated polybutadiene (HTPB) composite propellants have discovered that both AP and HTPB have an absorptivity efficiency to $10.6\text{ }\mu\text{m CO}_2$ laser radiation of 0.93 (Cain, 2006). MWCNTs have a very high laser absorption efficiency and oftentimes are added in small quantities to increase the absorption efficiency of a composite (Ramadurai, 2006; Ramadurai, 2008; Wencke, 2021). As a comparison, representative regression rates for a given heat flux for ECSP_0 and ECSP_3.75 when the electrodes are used to sustain combustion are shown in Fig. S2.17. The heat flux for these experiments was calculated by multiplying the current draw by the applied voltage potential to get the applied power and dividing this power by the average contact area between the propellant and the electrodes during combustion. The error bars for the electrode-based combustion represent the uncertainty of the measurements which was determined using the method developed Kline and McClintock (Kline, 1953). As shown in Fig. S2.17 the regression rate of the propellant when the electrodes are used is higher than when the laser is used for a similar heat flux. Assuming that the ECSP compositions in this study have an absorptivity similar to AP composite propellants (Cain, 2006), the electrode-based combustion still has a higher regression rate per absorbed heat. The higher regression rate for a similar heat flux illustrates how the electrochemical reactions are likely significant in increasing the regression rate. Whether the propellants were ignited by laser or by electrodes, while under atmospheric conditions, the propellant readily quenched once the additional power input was removed.

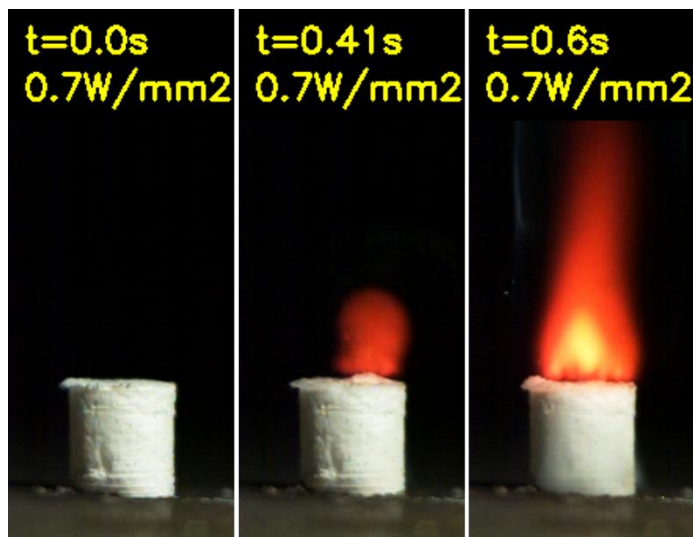


Fig. S2.16 ECSP_0 laser ignition and combustion with a 0.7W/mm^2 heat flux under atmospheric conditions

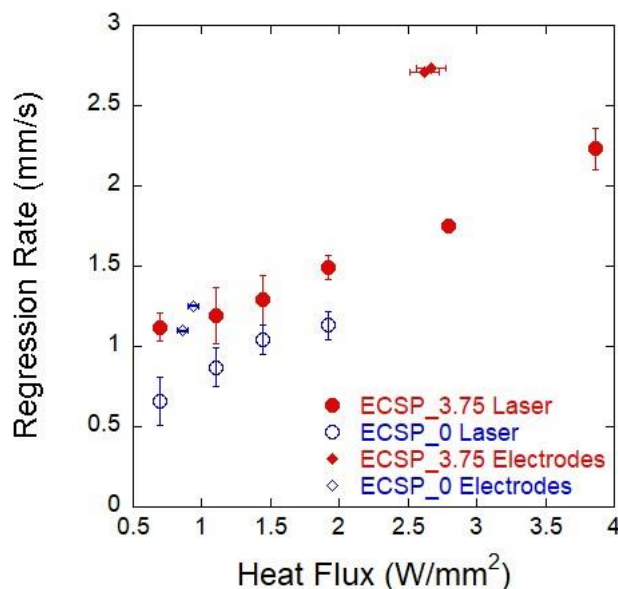


Fig. S2.17 Regression rate vs heat flux comparison for laser and electrode-based combustion

S2.2.5 Pressurized Experiments

The burning rates of the ECSP_3.75 and ECSP_0 were measured at elevated pressures for a pressure range of 0.4-1.5 MPa. ECSP_3.75 is conductive in its solid state and readily ignites when voltage is applied, however, ECSP_0 is not conductive in its solid state and requires the addition of a conductive medium to achieve ignition. For this study, a drop of water was placed across the top surface of the ECSP_0 sample in between the electrodes to hydrate the top layer enough to be responsive to the voltage. Once the ECSP_0 sample ignites, and a conductive melt layer is formed, the remaining propellant can burn under the applied voltage potential alone. The resulting regression rates (r_b) as a function of varying pressure (P) and voltage (V) are shown in Fig. S2.18. The error bars shown in Fig. S2.18 are the measurement uncertainty determined using the method developed Kline and McClintock (Kline, 1953). For both the ECSP_3.75 and ECSP_0 compositions, the regression rate increased as the pressure increased. ECSP_0 only sustained steady combustion at 200V and running experiments at lower voltage resulted in poor combustion regardless of the pressure under which the burning is taking place. For a constant voltage, the regression rate of ECSP_3.75 increased as the pressure increased with a power law relationship much like the St. Robert's burning law relationship seen in many propellants. ECSP_0 did not follow the St. Robert's burning law consistently across the whole pressure range of interest and instead had a different relationship for the lower pressure versus higher pressure conditions. Holding the pressure constant and varying the voltage in ECSP_3.75 results in a similar power law relationship where the regression rate increases as the voltage is increased as shown in Fig. S2.18. Combining the impact of the applied voltage and pressure on the regression rate yields a modified St. Robert's burning law shown in Fig. S2.19. This figure compares the calculated regression rate to the predicted regression rate where a perfect correlation between the experimental and predicted regression rates results in all values falling perfectly on the mean burning rate line. The vast majority of the experimental values fall within 10% of the predicted regression rates which illustrates that the modified St. Robert's law relationship accurately predicts the regression rate for ECSP_3.75.

While the ECSP_3.75 composition readily ignites at elevated pressures, quenching this propellant was not possible at pressures above 0.34MPa. Even decreasing the MWCNT concentration to the ECSP_2.5 composition had similar difficulty in quenching the propellant. Meanwhile, ECSP_0 when ignited with a hot wire ignition source or through the use of a conductive medium can be quenched at pressures up to

3.1MPa. The inability to quench the ECSPs with nanotubes is likely due to a combination of factors. First, the extremely high thermal conductivity of carbon nanotubes (Han, 2011) will increase the thermal conductivity of the propellant. Second, the catalytic impact of the MWCNTs as discussed in Section S2.2.1 may promote condensed phase decomposition more readily. Third, the inclusion of carbon nanotubes will increase radiation heat feedback from the flame zone, while at the same time increasing the absorption properties of the propellant. Thus, a propellant that both contributes and absorbs more heat from the flame zone is more difficult to quench.

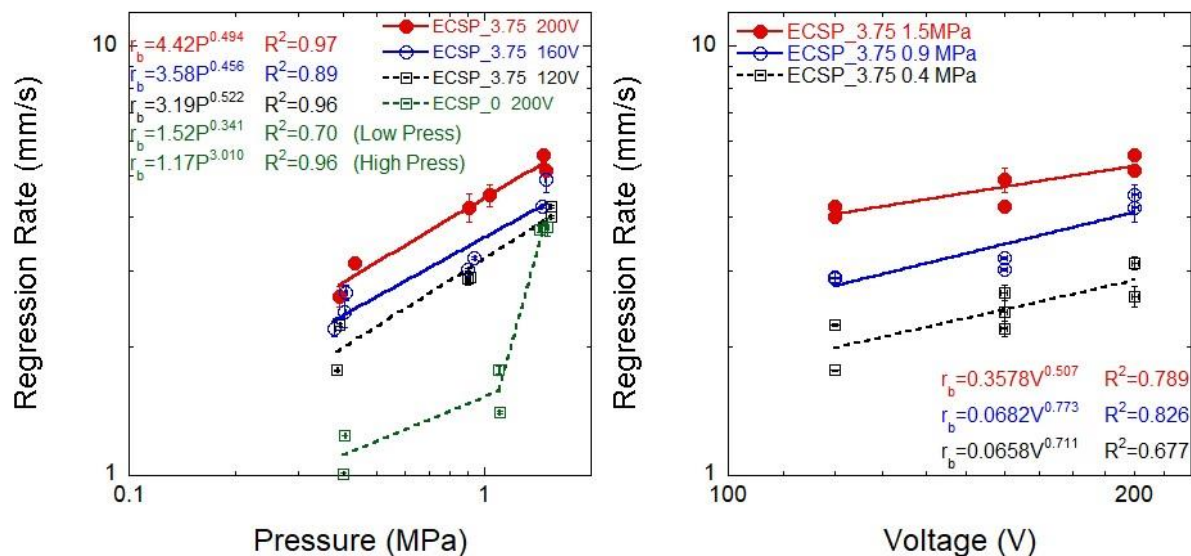


Fig. S2.18 Regression rate of ECSPs with constant voltage (left) and constant pressure (right)

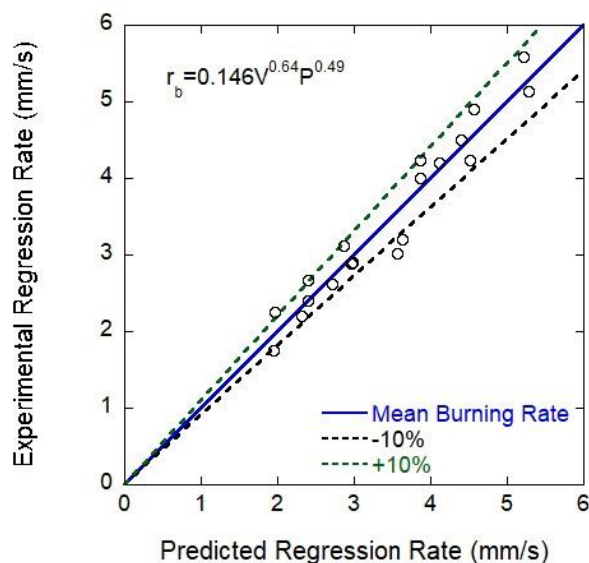


Fig. S2.19 Correlation of the predicted and experimental regression rate for ECSP_3.75

S2.3 Conclusion

An experimental study was conducted on ECSPs containing MWCNTs to analyze how compositional changes impact the ignition and burning characteristics of the propellants. These ECSPs use the electrically conductive nature of the MWCNTs to create a melt layer due to ohmic heating which then enables electrochemical reactions to occur. The addition of MWCNTs results in an accelerated decomposition occurring at a lower temperature when subjected to low heating rates as in a TGA environment. Increasing the MWCNT concentration and applied voltage also dramatically decreases the ignition delay of the ECSPs.

When subjected to elevated pressures, the ECSPs containing MWCNTs were found to readily ignite, but the combustion of these ECSPs self-sustain even under slightly elevated pressures. ECSP compositions without MWCNTs were found to extinguish at pressures of 3.1MPa and can be reignited with the reapplication of a voltage potential as long as the conductive melt layer was still present. However, these compositions without MWCNTs are not conductive in their solid state and require the addition of a conductive medium to enable the initial ignition. These results show that the addition of electrically conductive components into ECSPs enables the creation of highly responsive propellants, but the conductive additive must be carefully selected to enable quenching of the propellant at elevated pressures. The pressure and voltage under which the combustion occurs both impact the burning rate of the propellant and allow for additional control over the burning rate when compared to conventional solid propellants.

Solid Propellant Study 3 “S3”

This research builds on previous work which investigated the role of conductive additives in ECSP compositions. In this work, carbon black (CB) is investigated for the first time in ECSPs, and aluminum powder is considered as an additive in an attempt to promote both solid phase conductivity, and energy content. The impact of each additive is characterized in terms of response time and regression rate in both atmospheric and elevated-pressure environments at varying power levels. Limited experiments were performed with MWCNT additives to discern how morphological differences between carbonaceous additives affect ignition delay.

S3.1 Materials and Methods

S3.1.1 Conductive Additive Propellant Preparation

ECSPs were prepared from PEO, LP, additive, and acetonitrile. The PEO was purchased from Sigma Aldrich with a viscosity average molecular weight (M_v) of 200,000 g/mol. The LP and acetonitrile were purchased from Fisher Scientific and had stated purities of over 95% and 99% respectively. The CB was purchased from Fisher Scientific with stated purity of over 99.9%, and the aluminum powder (H2AL) was purchased from Valimet (2-3 μm diameter, 99.7% stated purity). The MWCNTs were purchased from Cheap Tubes with a stated purity of over 95%, length of 10-30 μm , and outside diameter of 10-20 nm. Scanning Electron Microscope imaging of additive materials was performed at the Virginia Tech Nanoscale Characterization and Fabrication Laboratory (NCFL) using the JEOL IT-500HR analytical Field Emission Gun - Scanning Electron Microscope (FEG-SEM). Representative images for each additive are provided in Fig. S3.1. The primary particle size of the CB is well below 1 μm but considerable agglomeration can be seen in the image. The majority of H2Al imaged falls close to the supplier given range, although some particles are observed to be 2-3x that. Relevant thermal and electrical characteristics of each additive are given in Table S3.1. Although not independently controlled, the selected additives vary by several orders of magnitude for each of the indicated properties.

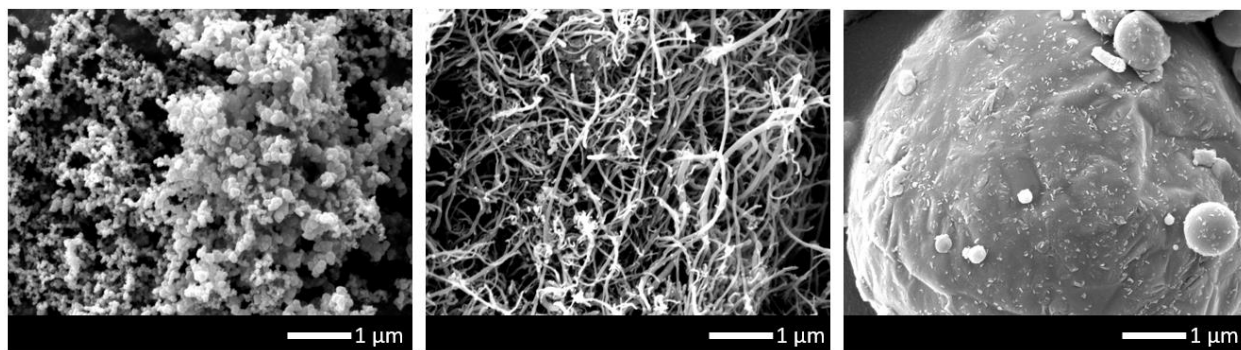


Fig. S3.1. Scanning electron microscope images at 20k magnification of each conductive additive: CB (left), MWCNTs (center), H2Al (right).

The ECSPs were synthesized by the solution casting method. The PEO and LP were first dissolved in acetonitrile to form a homogenous solution. The additive was then added into the solution and allowed to stir. The solution was stirred at 70°C until becoming too viscous and the stir rod seized. The solution was then poured into a Teflon tray and placed in a vacuum oven to dry under vacuum at 13 kPa and 70°C. The propellant samples were then cast into rectangular prism molds (12.7 mm x 12.7 mm x 40 mm) at room temperature to harden. After hardening, the propellants were stored under vacuum to prevent moisture absorption.

Table S3.1 Material properties of the additives

Additive	Specific Surface Area (m ² /g)	Electrical Conductivity (S/cm)	Thermal Conductivity (W/m-K)	References
CB	75	0.1 - 100	0.1 - 0.5	(Spahr, 2017)
MWCNT	233	10 ⁵	2000-6000	(Han, 2011; Huang, 2019; Kim, 2001)
AL	1.5	10 ⁵	236	(Cook, 1976; Jordan, 2007)

CB: Carbon black; MWCNT: Multiwall carbon nanotubes; AL – Aluminum.

S3.1.2 Propellant Compositions

A list of the propellant compositions is given in Table S3.2. The samples maintained ~25% PEO binder due to prior research indicating mechanical properties quickly degrade below this condition (Gobin, 2024). The CB additive was evaluated at 2.5% and 3.75% for direct comparison with prior work using MWCNTs (Gobin, 2024).

Table S3.2 ECSP formulations

Sample Name	Additive	wt% PEO	wt% LP	wt% Additive
CB1	Carbon Black	25	72.50	2.50
CB2			71.25	3.75
MWCNT1	MWCNTs	25	72.50	2.50
AL1	Aluminum	24	66	10

S3.1.3 Thermal Analysis

Prior experimentation observed that the addition of MWCNTs to LP reduced onset temperature of thermal decomposition (Gobin, 2024). Thermal decomposition experiments were performed on oxidizer/additive pairs using simultaneous differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). For these experiments, LP was dissolved into acetonitrile then the additive was dispersed into the solution. The ratio of LP to additive was consistent with the compositions listed in Table S3.2. The acetonitrile was then evaporated off by heating the solution on a stir plate at 50°C. The thermal analysis was performed using a Netzsch STA 449 F5 Jupiter at 10°C/min from room temperature to 800°. Nitrogen was used as the protective and purge gas during experimentation at flow rates of 50 mL/min and 20 mL/min respectively.

S3.1.4 Combustion Experiments - Ignition

Ignition experiments were performed in the fixture shown in Fig. S3.2a under atmospheric pressure for each of the propellants considered in this study. The posts, spacer, and base were fabricated from garolite to electrically insulate the experiment. Two stainless steel electrodes were mounted at the top of the fixture which delivered an electric potential across the ECSP sample. In our earlier work (Gobin, 2024), we used copper electrodes; however, as we progressed to pressurized experiments, we found that more robust materials were required. The electrodes angled inward 20 degrees from vertical to ensure that the ECSP sample maintained contact with the electrodes throughout the experiment. Using this same fixture, a series of experiments were also conducted to determine the propellant burning rates at atmospheric pressure for the PEO-based propellants.

The ECSPs were fed into the electrodes using springs which were compressed slightly before each experiment. The springs provided an upward force to keep the solid surface of the ECSP in contact with the electrodes and were aligned coaxially around guide rods to maintain the vertical orientation of the spacer and ECSP sample.

Experiments were performed by first loading in an ECSP sample, then attaching wires to the electrodes to the leads shown in Fig. S3.2. Once in place, an electric potential ranging between 140-200 V was applied across the ECSP sample using a DC Power supply. The voltage was measured from the power supply outlet and the current was measured using a Teledyne Test Tools T3CP100-2 current probe, both were recorded using a National Instruments USB-6363 data acquisition system.

A high-speed camera (Vision Research Phantom VEO 7.10L) was used during the experiments to capture the ignition process of the ECSP sample. The camera was triggered simultaneously with the power supply and was used to track the decomposition of the ECSP sample, primarily the melt layer development and progression prior to ignition. High-speed imaging was also used to identify changes in the ignition location and ignition delay. Time during the ignition experiments was measured from the camera trigger, and the ignition delay was defined as the time between the first frame and the first light observed.

S3.1.5 Combustion Experiments – Elevated Pressure

The combustion of the propellants was examined at elevated pressure by placing the fixture shown in Fig. S3.2a inside an optically accessible strand burner as shown in Fig. S3.2b to examine the combined effects of both input voltage and pressure. During these experiments, the strand burner was pressurized using nitrogen gas, after which a voltage was applied across the propellant surface. During the experiment, the pressure was gathered using a Setra 206 static pressure transducer. The regression rate of the propellant was determined using video to track the position of the propellant strand over time. The slope of this line was taken after the propellant had reached a steady burn and an average pressure was determined over the time interval.

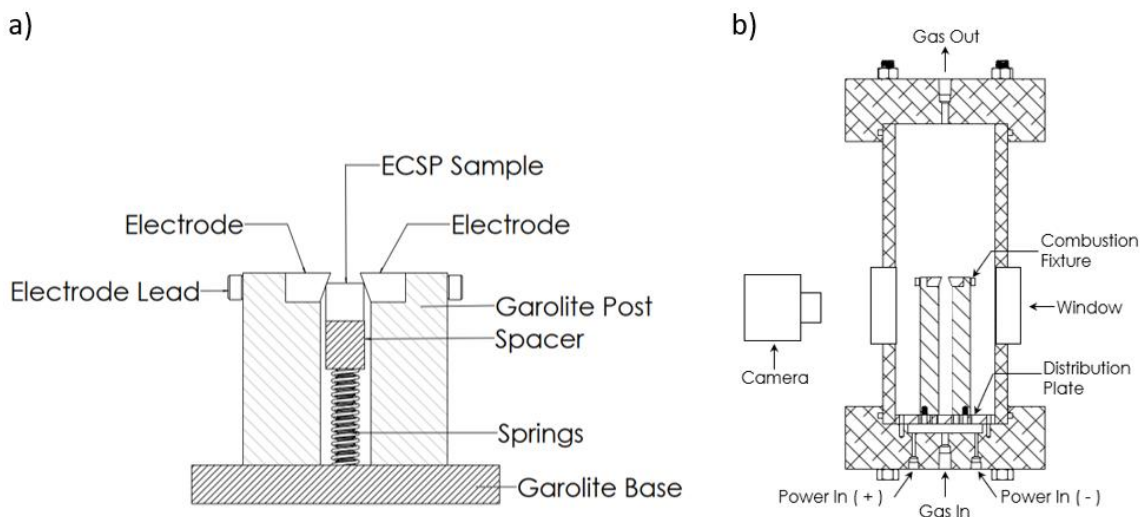


Fig. S3.2. Sideview of a) the combustion fixture and b) its integration into a strand burner for pressurized experimentation.

Experiments were also performed to determine the pressure deflagration limit (PDL) of each propellant. Prior to these experiments, the electrodes were removed from the combustion fixture, and a small piece of in house HTPB/AP composite propellant was secured to the ECSP samples using nichrome wire as an ignition source. The strand burner was pressurized after which the composite propellant would be ignited. The PDL was determined as the point where the ECSP would quench, and not self-sustain combustion to within 0.17 MPa.

S3.1.6 Combustion Experiments – Laser Assisted Combustion

Laser assisted combustion experiments were conducted to determine the regression rate of the ECSPs for comparison to electrically powered combustion under similar input heat fluxes. A schematic diagram of the experiment is shown in Fig. S3.3. For these experiments the propellants were formed into circular cylinders, 5mm in diameter and 10mm in length. The 5mm circular cross section was selected so the beam would cover the sample's cross section (Gobin, 2024). Experiments were performed by applying a prescribed heat flux to the propellant sample using a Coherent Inc. Diamond J-2 CO₂ laser (10.6 μm wavelength). The propellant regression was imaged using the same high-speed camera used for ignition testing throughout the experiment allowing linear regression rates to be determined.

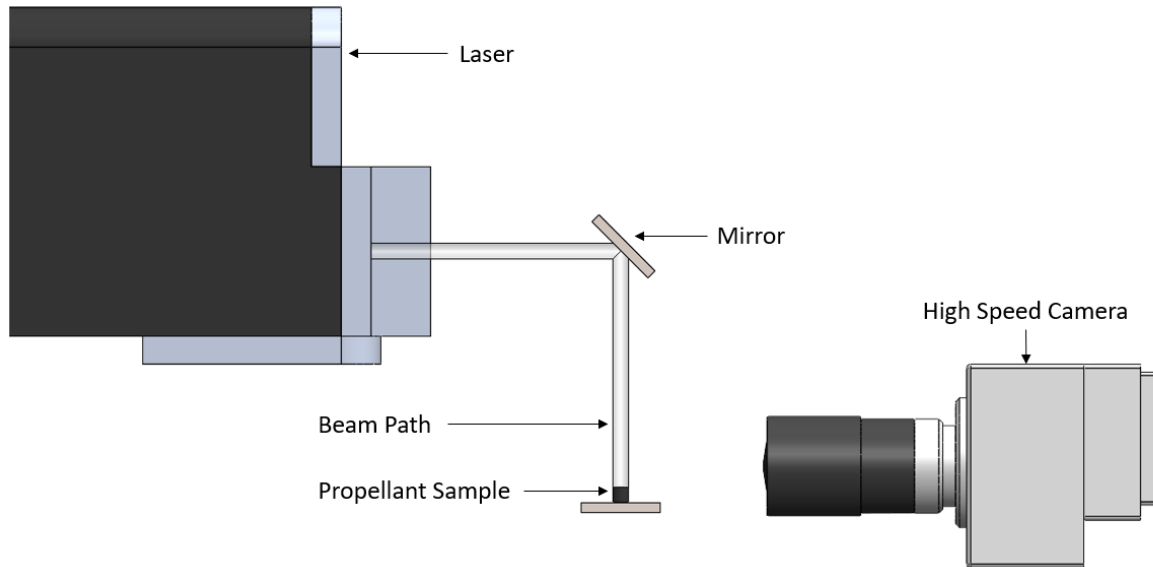


Fig. S3.3. Side view of the laser assisted combustion experiment.

S3.2 DISCUSSION OF RESULTS

S3.2.1 Effect of additives on ignition behavior

Fig. S3.4 shows a representative ignition experiment with CB1 at an applied voltage of 180 V. The images illustrate the primary decomposition steps leading to ignition of the sample; similar decomposition steps were observed for CB2 and AL1.

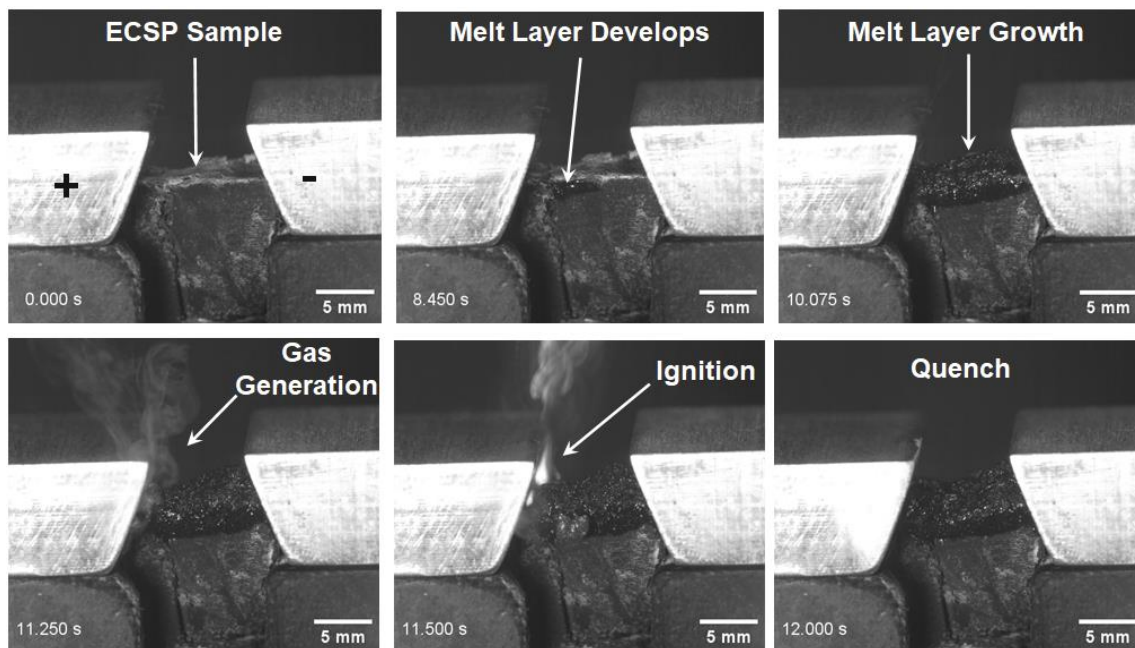


Fig. S3.4. Decomposition of CB1 in response to 180V applied voltage (anode left).

During the first 8 seconds of the experiment shown in Fig. S3.4 no physical changes were observed, however current was being drawn through the propellant. The ohmic heating from the current flow began to liquify the sample's surface after 8.4 seconds. Across all propellants, the surface liquefaction is concurrent with a sharp rise in current which is illustrated in Fig. S3.5. As the melt layer developed, gas started to evolve from the anode followed shortly after by ignition and flame propagation. After ignition was achieved, the voltage was removed, and the propellant quenched shortly after. An average ignition delay for each propellant is shown in Fig.S3.6a with error bars representing the standard deviation of at least 3 experiments. AL1 had ignition delays of near a minute and exhibited high variability below 180 volts and therefore the data is not presented.

The decomposition of CB1, CB2, and AL1 followed the same steps of ohmic heating leading to melt layer growth, gas evolution, and eventual ignition. The ignition of CB1 and CB2 occurred exclusively at the anode. This ignition sequence is similar to what has previously been observed in PEO/LP propellants with MWCNT additives (Gobin, 2024). AL1 ignited at both the anode and cathode on different experiments, although cathode ignition was infrequent. AL1 ignited at the cathode twice out of four experiments at 200 V and did not ignite at the cathode at lower voltage conditions. In experiments where cathode ignition was observed, substantial gas production was identified at both the cathode and anode which is not seen in the ignition process of CB1, CB2, or MWCNT1. Li et al. found that ignition location of ECSPs based on PVA and LP ignited was dependent electrode polarity, material, surface roughness and area ratio (Li, 2021).

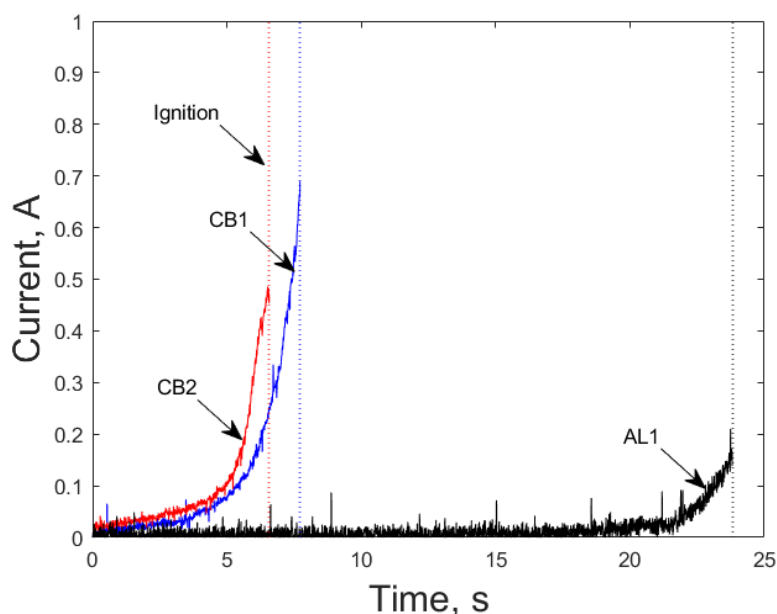


Fig. S3.5. Current draw during the ignition process of each ECSP at 200 V (voltage applied at $t = 0$ seconds).

As seen in Fig. S3.6a, higher CB concentration resulted in lower ignition times for CB2 compared to CB1. Increasing the concentration of carbon black increases the conductivity of the ECSP, particularly in the 2-10 wt% range (Spahr, 2017; Huang, 2002). The current draw for more conductive material is higher when voltage is applied causing more rapid heat generation which is described in Equation S3.1.

$$P = \frac{A V^2 \sigma}{L} \quad (\text{S3.1})$$

Here P is the power dissipated by a resistive element in a DC circuit, A is the contact area, V is the applied voltage, σ is the conductivity, and L is the distance between electrodes. Higher conductivity is directly

related to power dissipation and heat generation. The increase in heat generation causes the propellant surface to liquify faster allowing for electrochemical processes to proceed culminating in ignition. The current draw and ignition time for a sample of CB1, CB2 and AL1 are shown in Fig. S3.5.

The samples made with MWCNTs demonstrated lower ignition time compared to CB at the same concentration and applied voltage. Thus, morphological changes between the two materials must be responsible. MWCNTs have been shown to be more conductive than CB in polymer composites because of their high aspect ratio and specific surface areas allowing for longer conductive paths with more interfacial area to be formed (illustrated in Fig. S3.1) (Spahr, 2017; Brigandi, 2017). Additionally, MWCNTs have higher thermal conductivity which allows the heat to propagate more quickly through the propellant surface. AL1 samples had the longest ignition delay. The AL1 samples pulled the least current (Fig. S3.5) of all the propellant samples and were slowest to liquify and ignite. The ignition took more than 15 seconds on average to ignite at 200V, and the ignition delay rose quickly as applied voltage was reduced.

The inverse relationship between voltage and the ignition time in ECSPs has been established across a number of studies (Gobin, 2022b; Gobin, 2024; Li, 2023), and the same relationship exists for the results presented here. The ignition of ECSPs was observed strictly after a melt layer formed between the two electrodes. The melt layer is generated through ohmic heating and so the ignition process is limited by the rate of heat generation in the propellant which is the power consumption from Equation 1. Thus, the ignition time is inversely proportional to the power consumed by the propellant which encapsulates the relationship between ignition time, conductivity, and voltage (Equation S3.2).

$$t_{ign} \propto P^{-1} \propto \frac{1}{\sigma V^2} \quad (\text{S3.2})$$

Using Equation S3.2, the data should display a linear relationship between ignition time and the inverse of voltage squared. Additionally, Equation S3.2 predicts that increasing propellant conductivity would reduce the slope of the fit. Fig. S3.6b displays this behavior which lends credibility to the observation that ohmic heating is rate limiting in the ignition process.

The liquefaction of the propellant surface in experiments with conductive additives is distinct from prior research without conductive additives (Gobin, 2022b). In a study of PEO/LP ECSPs without conductive additives, Gobin et al. observed that the melt layer developed at the cathode in all experiments which was ascribed to the cathode instability of PEO at high voltages (Gobin, 2022b). Preferential melting at the cathode was not observed in this experiment; Fig. S3.4 shows melt layer development in the center of the ECSP sample.

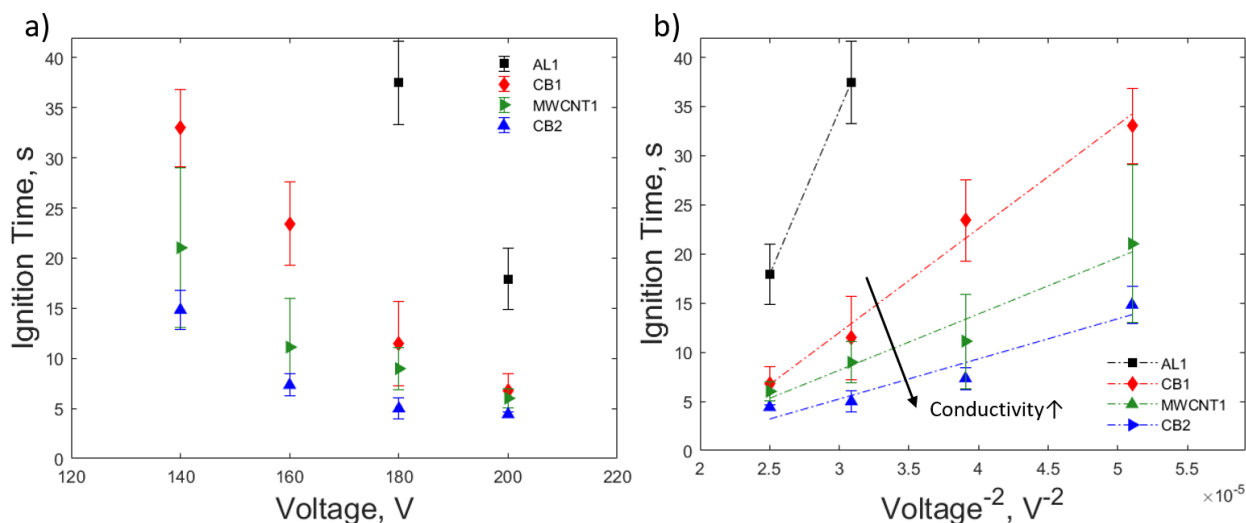


Fig. S3.6. Ignition delay for PEO based ECSPs with conductive additives arranged to show: (a) the inverse, non-linear relationship between voltage and ignition time (b) linear relationship between the inverse of voltage squared and ignition time.

S3.2.2 Atmospheric regression rates of ECSPs under electrical and thermal stimuli

Atmospheric combustion experiments were performed to compare the decomposition of the ECSPs in response to electrical and thermal stimuli with results shown in Fig. S3.7. The electrical heat flux shown is an average power over the course of the propellants burn divided by the electrode contact area (163 mm²). The electrode regression data in Fig. S3.7 has many data points below 0.75 W/mm² which is a consequence of low current draw during combustion. The laser heat flux was taken as the beam power across the propellant's cross-sectional area. Using the beam heat flux assumes an absorptivity of one and will overestimate the heat absorbed by the propellant. The absorptivity of an ammonium perchlorate, hydroxyl-terminated polybutadiene propellant investigated by Cain and Brewster had an absorptivity of 0.93 (Cain, 2006). Assuming absorptivity near this value and noting that the differences observed in this experiment were large, using the beam power is not expected to change the conclusions drawn from the data.

The heat flux applied through electrodes resulted in higher regression rates compared to the laser regression experiments; similar results were found in a study of MWCNT regression rates (Gobin, 2024). In this study, equivalent regression rates are consistently achieved at 30-50% lower heat fluxes under electrical stimulus. The increase in regression rate of solid oxidizers was investigated by Gobin et al. which clearly showed that ionic solid oxidizers like LP can be decomposed faster under an applied electrical stimulus compared to a thermal stimulus (Gobin, 2021). The electrochemical decomposition of the ECSPs is faster than thermal decomposition which confirms the electrochemical reactions are important to the decomposition process. A number of other factors support the conclusion that electrochemistry is important to the combustion process including preferential ignition at the anode, and combustion cessation upon voltage removal despite thermal feedback from the flame and residual heat from the electrodes.

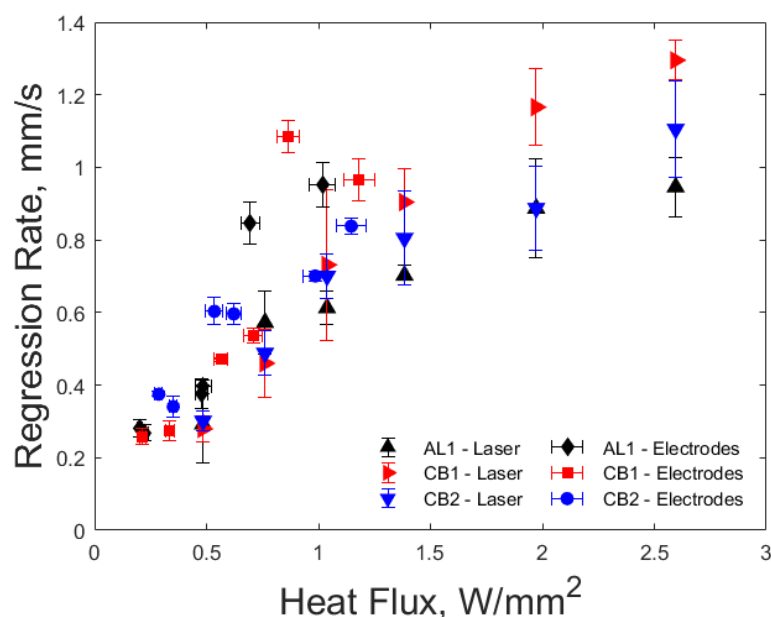


Fig. S3.7. Atmospheric regression rate tests for propellants from applied electrode and laser heat fluxes.

S3.2.3 Effects of voltage and pressure on ECSP combustion

Two series of experiments were conducted under elevated pressure. The first determined the pressure deflagration limit for each propellant composition to determine where the propellant could no longer be quenched. This is an important consideration for developing ECSPs as this is the point where the stop-start capability can no longer be achieved. The pressure deflagration limit for each propellant is given in Table S3.3 along with a PEO and LP propellants without additives (Gobin, 2024).

Table S3.3 ECSP pressure deflagration limits

Sample Name	PDL (MPa)	Reference
CB1	1.21	-
CB2	0.86	-
MWCNT1	0.34	(Gobin, 2024)
AL1	3.10	-
Neat PEO/LP	3.10	(Gobin, 2024)

The data show that carbon additives substantially reduce the PDL of the propellant, and aluminum does not impact the PDL of the propellant. The addition of MWCNTs serves to increase the thermal conductivity and absorptivity of the propellant, and Gobin et al. showed the MWCNTs have a catalytic effect on the decomposition of LP and lower the onset temperature of the LP's thermal decomposition (Gobin, 2024). Neither the addition of CB nor H2AL significantly reduced the thermal decomposition temperature of lithium perchlorate (Fig. S3.11). Using CB as an additive increases the PDL by nearly 4 times compared to MWCNTs at the same concentration. The reasons for this must stem from the different material properties of the carbon additives because they are atomically identical. CB has lower specific surface area and thermal

conductivity compared to MWCNTs which reduces the additive/salt interaction and heat propagation into the propellant respectively.

AL1 maintained the same pressure deflagration limit as the PEO/LP with no additives. This is a surprising result given that aluminum fuel is often used to increase the energy density of solid propellants. In the pressurized burn rate experiments shown in Fig. S3.8, aluminum regressed slower than ECSP formulations without additives which indicates that the aluminum was acting as a heat sink and removed more energy locally than it contributed to the combustion process (Gobin, 2024).

The second series of elevated pressure experiments sought to characterize the burn rate in response to elevated pressures, and variable power. In the ECSP literature, elevated pressure experiments are commonly performed at a single voltage which makes it difficult to ascertain the relative effects of voltage and pressure on combustion rates. In this work, experiments were performed on each propellant at nominal pressures of 0.35 MPa and 0.86 MPa at three voltages (120 V, 160 V and 200 V). CB1 was selected for experiments at a higher pressure condition (~ 1.3 MPa) because of its well behaved pressure exponent ($n < 1$) between the 0.35 MPa and 0.87 MPa conditions and comparatively low ignition delay. CB2 exhibited pressure exponent above 1, and AL1 had prohibitively long ignition delays which are unfavorable and so experiments at 1.3 MPa were not performed for these propellants. Burn rate data as functions of pressure is given in Fig. S3.8, along with a Saint-Robert's burn rate law at each distinct voltage.

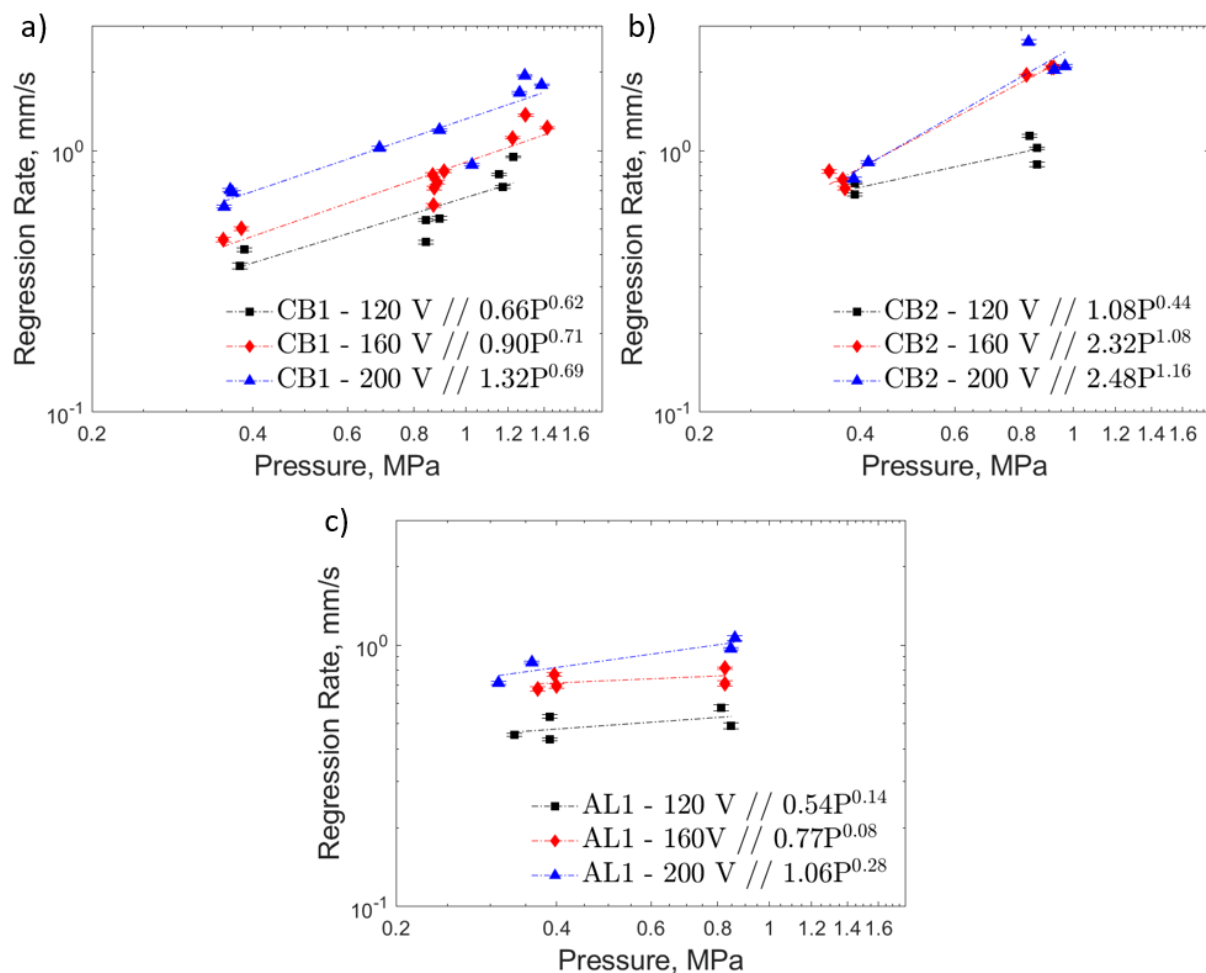


Fig. S3.8. Linear burn rates vs. average pressure at constant voltage for (a) CB1 (b) CB2 (c) AL1.

The regression rates of CB1 and AL1 were well stratified with increasing voltage; this stratification allows the propellant regression rate to be easily manipulated by changing the magnitude of the applied voltage. The 160 V and 200 V conditions for CB2 resulted in very similar burn rates and were not easily distinguishable. AL1 displayed the least sensitivity to pressure with exponents between 0.08 and 0.28, CB1 had higher pressure dependence near 0.7. The burn rates of CB2 at 160 V and 200 V exhibited pressure exponents greater than 1 which is generally undesirable since it increases the likelihood of pressure excursions in a motor. Prior experimentation has shown that in experiments up to 1.5 MPa, ECSPs with MWCNTs above their PDL do not have a pressure exponent above one (Gobin, 2024). The regression of all propellants proceeded very slowly with sub mm/s regression rates being common at 0.34 MPa and ~1 mm/s at 0.86 MPa for CB1 and AL1. CB2 burn rate was faster than the other two propellants, but still was only half as fast as experiments performed with MWCNTs (Gobin, 2024).

Fig. S3.9 shows regression rates as a function of voltage at constant pressure. The pressure indicated in the legend is the mean pressure across all experiments at the nominal pressure condition, thus there are slight differences between the indicated pressures.

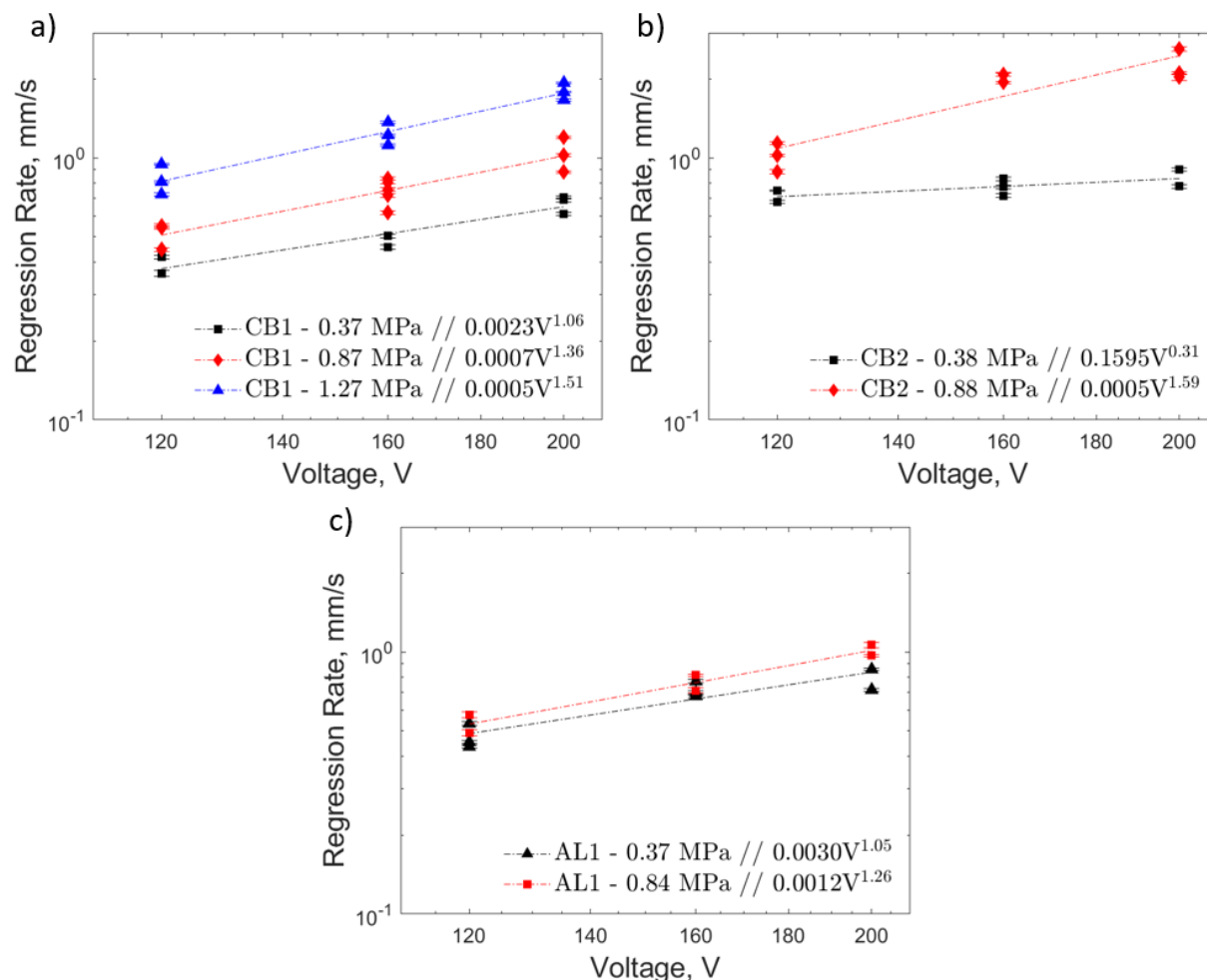


Fig. S3.9. Linear burn rates vs. applied voltage at constant pressure for (a) CB1 (b) CB2 (c) AL1.

Fig S3.9. illustrates a direct relationship between applied voltage and the regression rate in an elevated pressure environment. The voltage dependence at all conditions was on the order of 1-1.6 for all experiments apart from CB2 at 0.38 MPa which was fairly insensitive to voltage. The voltage dependence

increased with pressure for each propellant which indicates that pressure facilitates the electrical decomposition of the propellant sample. In this regime, as pressure increases, heat release occurs closer to the propellant surface and increased surface heating is likely to improve ion mobility in the melt layer leading to higher decomposition rates. Additionally, during the ignition studies, the melt layer of the ECSPs was large and filled with gas pockets. Elevated pressure would serve to compact the melt layer and increase current density (and therefore heat flux) in the melt layer. This may also be a result of higher electrode temperatures. It was noted that the change from copper to stainless steel electrodes was due to the copper electrodes melting during pressurized experiments. Therefore, there is significant thermal energy stored in the electrodes; the heat stored in the electrodes may begin to heat the propellant prematurely resulting in higher regression rates. The melt layer of the ECSP was not able to be monitored during combustion due to a large amount of smoke generation, but a combination of the factors considered is likely responsible for increasing voltage dependence.

Power law regressions accounting for both voltage and pressure are given in Table S3.4; the relationships show that the relative effect of voltage is stronger than the effect of pressure over the pressure range investigated in this work. This effect is unlikely to continue to higher pressure regimes where thermal feedback mechanisms are more pronounced. Zamir et al. observed a diminishing relative effect of applied power as pressure increased (Zamir, 2021).

Table S3.4 ECSP power law regressions incorporating voltage and pressure.

Sample Name	Power Law	R ²
CB1	$0.0013P^{0.67}V^{1.30}$	0.872
CB2	$0.0119P^{0.91}V^{1.00}$	0.856
AL1	$0.0022P^{0.18}V^{1.15}$	0.904

S3.2.4 Start-Stop-Start Capability

A significant advantage to ECSPs is their improved control authority over traditional solid propellants; their development has largely been motivated by the ability to throttle and gain start-stop capability. The effectiveness of these propellants requires that they be cyclable, and so stop-restart capability was demonstrated during these experiments. For this experiment, the propellant was first ignited and subsequently quenched by applying and subsequently removing an electric potential. After quenching the propellant sat for a period allowing the pressure to stabilize, then voltage was reapplied across the propellant and allowed to regress for a second period. Fig. S3.10 shows CB1 regression due to the applied potential. CB1 begins to regress after voltage application and regresses linearly until the voltage is removed. The flame sputtered for a short period then dissipated, though the propellant continued to regress for a longer period. The displacement between 25 and 35 seconds was caused by the propellant melting from the residual heat stored in the electrodes. After the propellant's movement had ceased, the voltage was turned back on, and the propellant began to regress once more. The end of the second regression occurred because the propellant feed mechanism reached the end of its stroke.

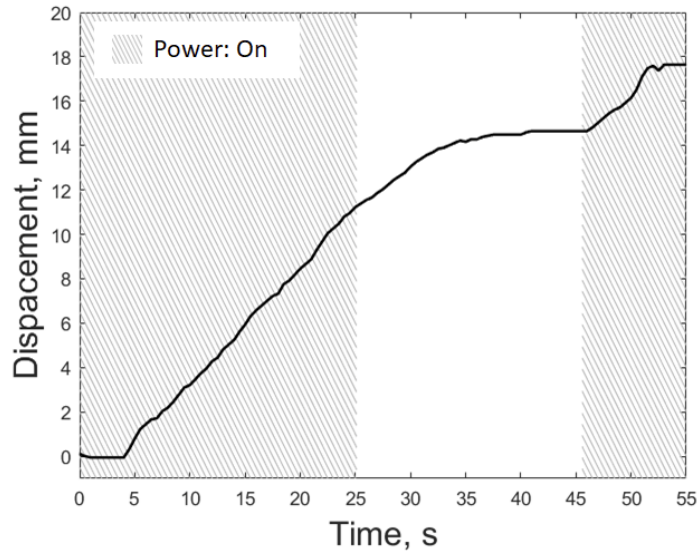


Fig. 3.10. CBI regression in response to applied voltage at 0.35 MPa.

The ability to turn the propellant on and off will be dictated by the PDL, above this point the propellant burns similarly to a solid propellant where the propellant will be completely consumed. Using MWCNTs as a conductive additive to this family of ECSPs lowers the PDL to 0.35 MPa and so MWCNTs, although a higher performing additive, may not be suitable for application in controllable solid rocket motors.

S3.3 Conclusions

A series of experiments were conducted to determine the impact of conductive additives on the ignition, combustion and quenching of electrically controlled solid propellants based on polyethylene oxide and lithium perchlorate. Experiments characterizing the ignition process showed that solid phase propellant conductivity and applied voltage are correlated with faster ignition times. This was attributed to increased current draw and heating rates which is consistent with results from past experimentation. The propellants were subjected to both electrical and thermal stimuli under atmospheric and elevated pressure to determine their influence on combustion rates. The propellants tested decomposed faster under electrical stimuli which supports the conclusion that electrochemistry is important in the melt layer and the propellant decomposition is not exclusively a product of ohmic heating. The effect of pressure and voltage on propellant combustion was summarized in Saint-Robert's burn rate type relationships. The pressure exponents for each propellant were markedly different showing that propellant combustion is sensitive to compositional changes and additive material properties. Finally, the quenching limits of each propellant were characterized; carbon additives substantially reduced the pressure deflagration limit, whereas adding aluminum did not change the pressure deflagration limit.

Incorporation of multiwall carbon nanotubes was shown to improve the voltage response of the propellants. However, the carbon nanotubes increased the pressure sensitivity of propellants and limited quenching to low pressures. Using carbon black as an additive extended the pressure deflagration limit of the propellants, but the propellants suffered from very low regression rates, and higher response times. Aluminum is also a viable option for maintaining solid phase conductivity. The aluminized propellants in this study were found to quench up to 3.1 MPa; significantly higher than the propellants with carbonaceous additives. However, the aluminized propellants had lower regression rates than propellants without additives and very long ignition delays at 200 V.

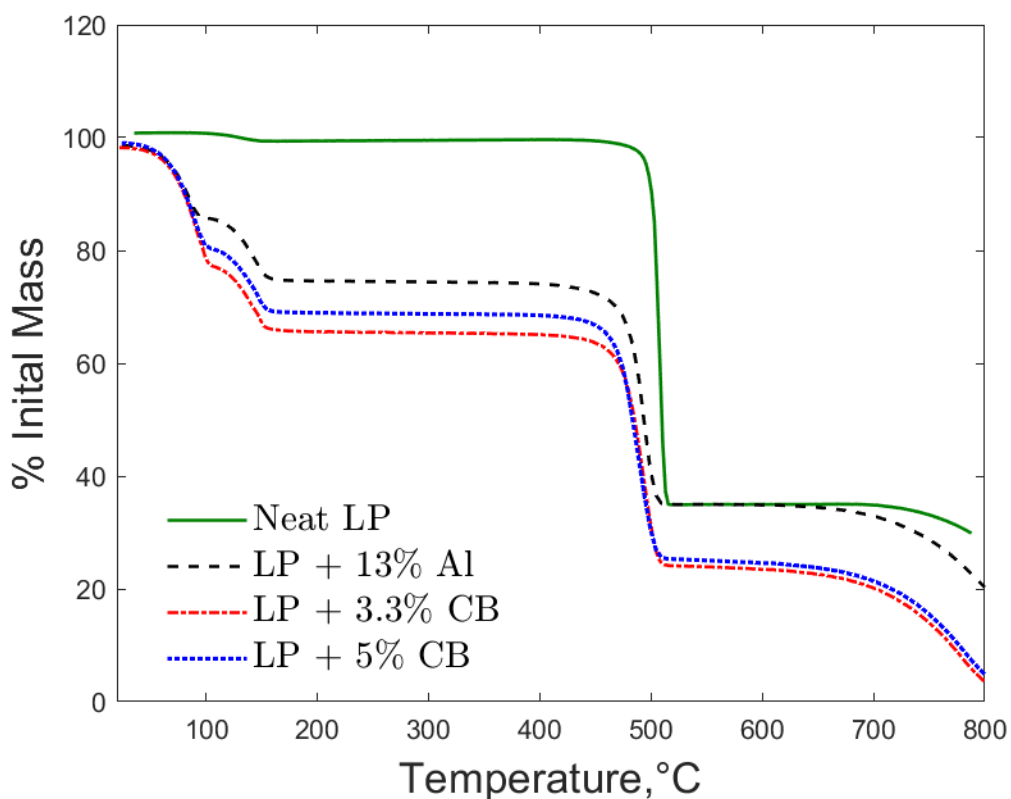


Fig. S3.11. TGA/DSC of neat lithium perchlorate and oxidizer/additive pairs. The low temperature decomposition ($< 200^{\circ}\text{C}$) is due to the evaporation of acetonitrile [13].

Dissemination

The research conducted in this effort has been presented at several conferences including AIAA SciTech and The International Symposium on Special Topics in Chemical Propulsion. Several peer reviewed journal articles have been published. Finally, we have communicated with representatives from the U.S. Air Force (Mr. Adam Brand) and the U.S. Navy (Dr. Jon Essel) about our work.

Impacts

Development of the principle discipline of the project

In this work, we have developed a basic understanding of the decomposition behavior of solid oxidizers when subject to electrical stimuli. This enabled the demonstration of both gel and solid propellants which can be initiated solely with the application of electrical power. The majority of the propellants discussed do not ignite when subjected to a butane torch. This behavior can allow for much safer propellants in the future. In addition, many of the propellants discussed have the ability to quench when electrical power is

removed, even at elevated pressure. The propellants studied provide an exciting groundwork for future propellants which can be readily throttled and extinguished.

Other disciplines

The work conducted in this study can be applied and related to current research on polymer electrolyte batteries. It provides important information regarding their flammability and safety.

Changes

Changes in approach

N/A

Problems or delays

There were no significant problems or delays

Expenditure Impacts

There were no significant expenditure impacts

Significant changes in the use or care of human subjects, vertebrate animals and/or biohazards

N/A

Changes to the primary place of performance from that originally proposed

N/A

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